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CHEMISTRY

FOR

DENTAL STUDENTS

VOLUME I

QUALITATIVE ANALYSIS AND DENTAL METALLURGY

BY

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FOURTH EDITION, REVISED AND ENLARGED

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PREFACE TO VOL. I, FOURTH EDITION

The Fourth Edition of "Chemistry for Dental Students" appears in two volumes, for the greater convenience of the student, who is not expected to-day to cover the subject in one or even two years, as he was when the earlier editions were published.

Volume I is designed to meet the requirements of the dental student in *Inorganic Chemistry*, taking up in detail qualitative analysis, with special emphasis on analysis of alloys, dental metallurgy, and sufficient volumetric analysis to familiarize the student with the methods applicable to the quantitative analysis of alloys and many dental preparations.

The aim of this volume is primarily to give to the beginning dental student such fundamentals in the study of Chemistry as have a direct bearing on Dentistry and will enable him to gain a clearer understanding of the subsequent work.

The outline character of the previous editions has been maintained, and the student is expected to have access to more complete works, such as

Qualitative Analysis, Stieglitz

Qualitative Analysis, Prescott & Johnson

Dental Metallurgy, Hepburn or Essig

H. C. S.

R. M. S.

TO THE STUDENT

As the student of dentistry takes up the study of chemistry, he should realize that the course will be of value to him in the ability acquired to draw correct inferences from observed phenomena, and in the attainment of accuracy and delicacy in manipulation, fully as much as in amount of chemical knowledge attained. In other words, he must do his own thinking, carry out his own processes and experiments, make his own analyses, or the time spent will be little better than wasted, for the chemical facts which he may happen to remember will be of slight benefit in the work to which every student, worthy of the name, aspires, that of developing, broadening and elevating the profession which he has chosen as his own.

The course of study outlined in this book is designed to furnish the starting-points, which will be of practical value in solving the problems constantly presenting themselves for consideration in the various branches of Chemistry. It is hoped that these starting-points may, in the future, serve as the basis for work along the lines of original research and that the best interests of dental science may be furthered thereby.

It is supposed that the student has had the advantage of a laboratory training in General Chemistry and is conversant with the properties and methods of preparation of the so-called non-metallic elements, also with the fundamental principles and laws of Theoretical and Physical Chemistry; that he is familiar with laboratory apparatus, such as test-tubes, beakers, crucibles, casseroles, evaporating-dishes, retorts, etc., and that he has had some experience in the ordinary processes of precipitation, filtration, evaporation, distillation, sublimation, and crystallization.

If there is any feeling of insufficient preparation, it is strongly advised that a short course of preliminary study be taken.

Chemistry furnishes the groundwork of all branches of medical science to a much greater extent than we are apt to think, and even in the study of subjects which in times past have been carried on with little reference to Chemistry, we now see the desirability, if not the necessity, of a good general knowledge of chemical science. The physiologist and the bacteriologist are to-day turning to Chemistry for the ultimate solution of their most perplexing problems.

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DENTAL CHEMISTRY

INTRODUCTION

Every science has a language peculiar to itself, a thorough understanding of which is an essential preliminary to the study of that science. Hence, before we take up the study of Dental Chemistry, it will be well to review a few definitions and perhaps a few of the facts of Physics which are closely related to our subject.

DEFINITIONS

Matter has been divided into masses, molecules, atoms and electrons, and we are to study first the properties of these divisions. For the purposes of present definitions it may be necessary only to consider that aggregations of electrons constitute atoms, groups of atoms make up the molecules, and numbers of molecules held together by the physical force of cohesion form masses.

Electrons are the infinitesimal particles of which the atoms are composed and have been regarded as constituting the force which determines their character. The present conception of the atom is that of a group of negative electrons around a much larger positive nucleus. The late Professor Harry C. Jones has explained the rôle of the electrons in the phenomenon of dissociation as follows.

“Take a salt like potassium chloride. When it is thrown into water an electron passes from the potassium over to the chlorine. The chlorine having received an additional electron thus becomes charged negatively, while the potassium having lost an electron becomes charged positively. If we are dealing with bivalent ions we have simply a transfer of two electrons. Take barium chloride. The barium loses two electrons, one to each of the chlorines; the latter becoming charged negatively, while the

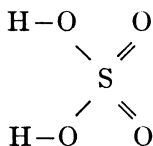
barium has, consequently, two positive charges upon it." The mental picture may be difficult but it is very necessary.

Valence. — Valence is a property of atoms and represents their combining power relative to hydrogen, measured, perhaps, by loss or gain of electrons. Valence is not always constant for the same elements; for example, sulphur has a combining power of six in sulphuric acid, of four in sulphur dioxide and of two in hydrogen sulphide. Nitrogen has a combining power of three in ammonia gas and five in ammonium chloride. Valence has also been indicated by the terms quantivalence and atomicity.

Chemical Formula. — A chemical formula represents the molecule and is made up of the symbols of the several constituent elements. Chemical formulæ may be empirical, dualistic or graphic. The empirical formula represents the molecule without reference in any way to its structure, i.e., H_2SO_4 .

The dualistic formula indicates compounds which may enter into the composition of a molecule. By this sort of formula sulphuric acid would be represented by $\text{H}_2\text{O}.\text{SO}_3$.

The graphic formula attempts to show the probable relation of the atoms in the molecule by means of bonds, e.g.,

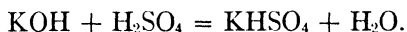


Acid. — An acid is a compound capable of producing, upon ionization, positive hydrogen ions which may be replaced by a metallic element or radical. The more common acids are sour to the taste and act in a characteristic manner upon a number of color compounds known as indicators

Base. — A base is a substance capable of producing, upon ionization, negative hydroxyl ions which may be replaced by acid radicals. The general characteristics of bases are opposite to those of acids. The strongest bases are known as alkalies, e.g., KOH , NaOH .

Salt. — A salt is a substance produced by the chemical union of an acid and a base.

In the formation of the salt, the acid may not have been completely neutralized by the base. In such a case the result is an *acid salt*, containing a part of the hydrogen ions of the acid, e.g., potassium acid sulphate, KHSO_4 , the production of which may be represented by the equation



Acid salts may or may not have acid properties, such as the sour taste and the power to give acid reactions with indicators. An example of the absence of these properties is NaHCO_3 , which is chemically an acid salt, but is alkaline to litmus and has other physical properties of the bases. This fact is explained by the hydrolysis of the salt (page 17).

The term **phase** refers to the condition in which a substance exists: solid, gaseous, liquid, crystalline. So sulphur is said to exist in four phases, and water in three.

The tables and laws given below may be useful to the student for reference.

Boyle's Law. — The volumes occupied by a sample of any gas are inversely proportional to the pressure at each volume.

Charles' Law. — The volumes occupied by a sample of gas at different temperatures, the pressure remaining constant, are in the same proportion as the corresponding absolute temperatures.

Gay-Lussac's Law of Combining Volumes. — Whenever gases unite, or gaseous products are formed, the proportion by volume (measured at the same temperature and pressure) of all the gaseous bodies concerned can be represented very accurately by small integers.

Avogadro's Hypothesis. — Equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules.

WEIGHTS AND MEASURES

Measures. — The metric system of weights and measures and the Centigrade thermometer are largely used in all scientific work. The dentist, however, has also considerable use for troy

weights and apothecaries' measures if he considers at all the composition of his gold solders, dental alloys, mouth washes, local anesthetics, etc. Hence, a few equivalents are here given.

The *meter* is the primary unit of the metric system and was originally calculated as one ten-millionth part of the quadrant from the equator to the pole.

1 meter = 100 centimeters = 1000 millimeters or 39.37 inches.

1 centimeter = $10/25$ or 0.3937 of an inch.

1 cubic centimeter = 16.23 minims or 0.0338 of a fluid ounce.

1000 cubic centimeters (c.c.) = 1 liter or 2.113 pts.

The weight of 1 c.c. of pure water at the temperature of its greatest density (4° C.) is taken as a unit of weight and called a gram (gramme).

1 gram = 15.43 grains.

1000 grams = 1 kilogram (kilo) = 35 oz. 120 grains or 2.2 lbs. avoird.

1 inch = 2.54 centimeters or 25.4 millimeters.

1 oz. av. = 28.3495 grams or 437.5 grains.

1 fluid oz. = 8 fluid drams, 29.57 c.c., or 456 grains of water.

1 fluid dram = 3.7 c.c.

1 troy oz. = 8 drams (ʒ) or 480 grains.

1 troy oz. = 24 scruples (ʒ) or 20 pennyweight (pwt. or dwt.).

1 scruple = 20 grains, 1 pennyweight = 24 grains.

1 grain = 64 milligrams.

1 pint = 473.11 c.c.

1 gallon = 8 pints, or 3785 c.c., or 231 cubic inches.

1 lb. avoird. = 7000 grains or 453.59 grams.

Measure of Temperature. — We shall constantly meet reference to both the Centigrade and Fahrenheit scales, and an understanding of the relationship of the two is essential.

The thermometer is graduated by marking the point at which the mercury stands when the instrument is placed on melting ice, and also the point reached by the mercury when the ther-

mometer is surrounded by dry steam under ordinary atmospheric conditions.

On the Centigrade thermometer, the lower (or freezing) point is marked zero, the upper (or boiling) point is marked 100, and the intervening space divided into 100 equal degrees. On the Fahrenheit scale, these points are marked respectively 32 and 212, and the scale is divided into 180 degrees; hence, $1^{\circ}\text{C. equals } 1.8^{\circ}\text{ or } 9/5^{\circ}\text{ Fahrenheit}$, and $1^{\circ}\text{F. equals } 5/9\text{ of a Centigrade degree}$. Providing for the different freezing points (0° and 32°), we can formulate a rule for converting temperature records from one scale to the other, as follows:

To convert Centigrade to Fahrenheit, take $9/5$ of the given number of degrees and add 32.

To convert Fahrenheit to Centigrade, subtract 32 from the given number and take $5/9$ of the remainder; e.g.,

$$\begin{aligned} 20^{\circ}\text{C.} &= 68^{\circ}\text{F.} \\ - 5^{\circ}\text{C.} &= + 23^{\circ}\text{F.} \\ 77^{\circ}\text{F.} &= 25^{\circ}\text{C.} \\ 14^{\circ}\text{F.} &= - 10^{\circ}\text{C.} \end{aligned}$$

Absolute Temperature

According to the Law of Charles, gases (free molecules) contract $1/273$ of their volume, measured at 0°C. , for every Centigrade degree that the temperature falls; so it is assumed that, at a point 273° below the Centigrade zero, no further contraction would be possible, molecular motion would cease, and all things become solid. This temperature has been called the absolute zero, and temperature recorded from this point absolute temperature; thus, water freezes at $273^{\circ}\text{C. absolute temperature}$.

GRAVITY

Specific gravity is the relative weight of equal bulks of different substances, one of which is taken as a standard.

The standard is usually water for liquids and solids.

The standard for gases may be air or hydrogen.

When gases are referred to hydrogen as a standard, the term

density is often used instead of specific gravity, and, to avoid confusion, this usage is recommended; i.e., the density of carbon dioxide is 22, while its specific gravity compared with air is about 1.53.

The density of a gas will, according to the Law of Avogadro, be one-half its molecular weight.

The specific gravity of a liquid may be diminished by the solution of a gas, as in case of solution of ammonia; or it may be increased, as in case of solution of hydrochloric acid.

The boiling point of a liquid is raised by the solution of solids, and often by the solution of gases.

CRYOSCOPY

The freezing point of liquids is lowered by the solution of other substances. As the amount of reduction of temperature necessary to change the liquid to the solid has been found to be in direct proportion to the amount of dissolved substance, it becomes possible to make many valuable determinations by this method. For accurate work, it is necessary to use a special thermometer graduated into hundredths of a degree. The use of the freezing point of a solution in determining the amount of the dissolved substance is known as cryoscopy, and is of great importance in both physical and physiological chemistry.

CHAPTER I

FUNDAMENTAL PRINCIPLES

IONIZATION

In studying ionization and the facts on which the theory of ionization has been built, let us first review briefly Avogadro's hypothesis in regard to gaseous volumes. This hypothesis, as stated in the Introduction, tells us that "equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules," and from this it follows that the molecular weight of all substances in the gaseous phase will occupy the same volume, i.e., 22.4 liters. With this hypothesis, which is practically a law, as a basis, comparatively simple and accurate methods for the determination of molecular weights of gases have been devised.

Van't Hoff extended Avogadro's hypothesis and attempted to apply it also to dilute solutions, saying that dilute solutions, under the same conditions of temperature and osmotic pressure, contain the same number of molecules. In proving his theory he encountered obstacles which finally have led to the Theory of Ionization.

The determination of the molecular weight of chloroform, ether, carbon bisulphide and several other compounds gave the *same* result whether the substance was in a *gaseous* state or in *solution*, but a large number of compounds were found to give abnormally low results when the determination was made with the substance in solution. Hydrogen chloride was an example of this group. Determined in the gaseous condition, hydrogen chloride has a molecular weight of 36.5, while, if the determination is made with hydrogen chloride in solution, the result will be much less and will tend to approach 18.25 as the solution becomes more dilute. Furthermore, those substances which failed to follow Van't Hoff's hypothesis were found to be the sub-

stances which, in solution, were capable of conducting an electric current — i.e., electrolytes — while those which gave normal results, chloroform, ether, etc., were found to be non-electrolytes.

As an explanation of these facts, Arrhenius has given us the Electrolytic Dissociation Theory, or the Theory of Ionization. Stated briefly, the main assumptions of this theory are as follows:

- (1) When an ionogen* is dissolved in water its molecules dissociate into *ions* and this process is known as “ionization.”
- (2) These ions carry either a positive or a negative charge of electricity, and the sum of the positive charges is always equal to the sum of the negative charges, making the solution as a whole electrically neutral.
- (3) The degree of ionization of a substance is inversely proportional to the concentration of the substance in solution, or, expressed differently, the more dilute the solution the greater the degree of ionization.
- (4) The dissociated ions of the molecule are capable of migration and will collect at the poles of a battery according to the well-known laws of magnetic attraction: the positive ion (cation, or metal ion) goes to the negative pole, while the negative ion (anion, or acid ion) goes to the positive pole.

This electrolytic dissociation of a molecule into ions, and also the tendency of the ions to reunite, may be clearly expressed as follows:

- (1) $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$
- (2) $\text{NaOH} \rightleftharpoons \text{Na}^+ + \text{OH}^-$
- (3) $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2^+ + \text{SO}_4^{--}$
- (4) $\text{FeCl}_3 \rightleftharpoons \text{Fe}^{+++} + \text{Cl}_3^-$
- (5) $\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + (\text{CH}_3\text{COO})^-$
- (6) $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

It will be noted that the strong acids, the strong bases, and most salts are highly ionized — that is, the tendency of the molecule to dissociate is considerably greater than the tendency of the ions to reunite; while in the case of a weak acid or a weak base, (5)

* An ionogen is a substance capable of producing ions — an electrolyte.

and (6), the reverse holds true. The degree of ionization of an acid or a base, therefore, is a true index of the strength of that acid or base. We would naturally expect this to be true from our fundamental definitions of acids and bases, a substance capable of yielding positive hydrogen ions being an acid and a substance capable of yielding negative hydroxyl ions being a base. With the Theory of Ionization before us, we must think of a solution of any inorganic substance as containing both unionized molecules and positively and negatively charged ions, and of this dissociation of molecules and reuniting of ions as an active process influenced by outside agents.

Ionization and Electrical Conductivity. — When hydrogen chloride gas is dissolved in water, a solution of hydrochloric acid, which is a good conductor of electricity, is produced. This may easily be shown by placing two electrodes connected with an electric bulb in the solution. The bulb lights almost immediately, demonstrating the passage of the current through the solution. A solution of sodium chloride gives practically the same result; with a solution of acetic acid, it is necessary to move the electrodes closer together to obtain a light; and with a sugar solution they must practically touch each other. On the basis of the Ionization Theory these facts are easily explained. Hydrochloric acid and sodium chloride are highly ionized and therefore their solutions have a high electrical conductivity. Acetic acid is less highly ionized and a poorer conductor of electricity, while sugar does not ionize to any appreciable extent and is a non-conductor of electricity.

Ionization and Determination of Molecular Weights. — In a preceding paragraph it was stated that the Ionization Theory was developed out of a failure to obtain correct molecular weights of a large class of substances in solution. Let us see just how this theory explains the abnormal results obtained. When hydrogen chloride ionizes, the molecule dissociates into *two ions* and each ion may be considered as acting more or less *independently* in the determination of the molecular weight. We should expect then to get an abnormally low result, tending toward one-half the true molecular weight, and this is exactly what was

actually obtained. Zinc chloride, a molecule dissociating to give *three* ions, will in like manner give a result tending toward one-third the true molecular weight.

Equilibrium. — The term equilibrium conveys the idea of equality between opposing forces, resulting in stability, e.g., the water in a closed bottle tends to evaporate; the tension or pressure of the vapor tends to prevent evaporation. When the one force equals the other, equilibrium results. Another example, illustrating the meaning of physical equilibrium and at the same time showing why concentration is so often useful in producing precipitates which may be easily filtered, is given by Stieglitz,* as follows: "If a crystalline precipitate is in contact with a solvent, e.g., if barium sulphate is in contact with the liquid from which it has been precipitated, then this liquid must be continually in a state of change, not of equilibrium, with respect to the solution and the deposited barium sulphate. The more minute crystals, being a little more soluble than the larger ones, will supersaturate the solution in respect to the larger crystals and the excess will be deposited on these larger crystals and make them grow still larger. This deposition will make the solution unsaturated with respect to the smaller crystals and more of these will dissolve. The process is obviously a continuous one, and must lead in time to the disappearance of the minute crystals and the growth of the larger ones."

As illustrated above, physical equilibrium is the equilibrium existing between *two phases* of one substance. The equilibrium existing between two or more chemical substances is perhaps more important for us, and we shall confine ourselves here to a brief consideration of this form of equilibrium — chemical equilibrium.

First, let us study the following reactions:

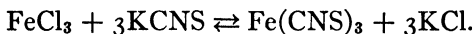
- (1) $\text{HCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{HNO}_3$
- (2) $2\text{HCl} + \text{Zn} \rightarrow \text{ZnCl}_2 + \text{H}_2$
- (3) $\text{HCl} + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{NaCl}$
- (4) $\text{HCl} + \text{NaNO}_3 \rightleftharpoons \text{HNO}_3 + \text{NaCl}$

* Qualitative Chemical Analysis.

Note that in the first two cases one product obtained by the reaction is of such a character that it is thrown out of the solution, as it were; in the third case one product is water, chemically inactive in the majority of cases; while in the fourth case two soluble products are formed. In the first three cases the two original substances will react until either one or the other has been exhausted, or, in other words, the reaction will go to completion. A completed reaction may be defined as one in which one product is either water or a substance which is removed from the solution either as a gas or as an insoluble precipitate.

The fourth reaction gives two soluble products; we find here a tendency for the reaction to go backwards — it is a reversible reaction — and this fact has been indicated by the two arrows. When the *opposing tendencies of a reversible reaction are equal*, a condition of chemical equilibrium is reached; or, using the type reaction $A + B \rightleftharpoons C + D$, equilibrium is established when the velocity of $A + B$ to form $C + D$ (V_1) is equal to the velocity of $C + D$ to form $A + B$ (V_2). Since the velocity of a reaction is dependent on and proportional to the concentration of the reacting substances, we may further say that $V_1 = [A][B]$ and $V_2 = [C][D]$, the bracketed symbols representing concentrations. Putting the two equations together, we have $\frac{V_2}{V_1} = \frac{[A][B]}{[C][D]} = K$, K being called the equilibrium constant.

As we might expect, a condition of equilibrium can easily be disturbed by the addition to the solution of any one of the four substances involved. If it is disturbed in this way, the force of the reaction will be increased in the direction necessary to bring about another condition of equilibrium satisfying the new concentration. This is clearly demonstrated in the following experiment.



If dilute solutions are used, so that only a trace of $\text{Fe}(\text{CNS})_3$ is formed, the addition of either FeCl_3 or KCNS will immediately produce a deeper red, while the addition of KCl will cause the solution to become nearly colorless.

Equilibrium and Ionization. — In the same way that we may think of a reaction as being in a state of equilibrium, we may think of the ionized and unionized molecule as existing in a condition of equilibrium. Such a condition would be expressed by the following ratio, acetic acid being used as an example:

$$\frac{[\text{CH}_3\text{COO}^-] \times [\text{H}^+]}{[\text{CH}_3\text{COOH}]} = K \text{ ionization}$$

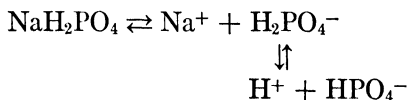
where the bracketed formulæ, as before, represent *concentrations*.

Ratios of this type, showing the relation between the ionized and unionized molecules, have been proved to be constant, and mathematical values, known as ionization constants, have been calculated. These constants are in direct proportion to the strength of the acid or base and also to the hydrogen-ion concentration of the acid or base. For all weak acids and bases, very accurate results have been obtained, but it must be noted that strong acids and bases and most salts do not give constant values. The reason is still open to inquiry.

If the ionization equilibrium is disturbed by increasing the concentration of one of the ions present, there will be a tendency toward the formation of more unionized molecules and the consequent restoration of the condition of equilibrium. For example, suppose some sodium acetate is added to a solution of acetic acid; an increase in the concentration of the acetate ion is effected, and this causes an increase in the formation of unionized acetic acid and a subsequent diminution of the concentration of the hydrogen ion. This can be demonstrated by the presence of a drop of indicator, which will be sensitive to the decrease of the hydrogen ion (Exp. 26). Precipitation will occur when the solution becomes more than saturated with unionized molecules. (See note, page 16.) The addition of a foreign electrolyte increases the *ionizing power* of the substance in solution and consequently, in the case of a weak acid, increases the actual concentration of the hydrogen ions in the solution (Exp. 24).

ACIDITY

The acid strength, or the acidity, of any solution is obviously dependent on the number of hydrogen ions which it has in solution. These hydrogen ions may come from free acid or from an acid salt yielding free hydrogen ions upon ionization. Thus, sodium acid phosphate ionizes according to the following reaction:



and free hydrogen ions are produced which give the salt its acid reaction. The existing acidity of a solution is due to the concentration of hydrogen ions present, and is expressed logarithmically as the P_H . Two standard methods are in general use for determining the hydrogen ion concentration of a solution, one of which will be explained in detail in our physiological work (page 161), of Vol. II.

The determination of this so-called existing acidity of body fluids is of great value in the study of a general systemic condition, because it very readily gives reliable information concerning the patient's tendency toward acidosis, whereas results from titratable acidity must be more or less conjectural.

Titrateable Acidity.—When an unknown acid solution is titrated against a standard alkali, the titration takes place progressively. The first few cubic centimeters of alkali added will neutralize the *ionized* acid which is present in the solution. This will then allow more molecules of acid to ionize, and the next portion of alkali added will neutralize the additional ionized acid. Eventually all of the unionized acid will have become ionized and then neutralized by the alkali, and the end point of the titration will be reached. From our previous knowledge we know that it is only the *ionized molecule* which is active chemically, so that acidity results obtained by titration are necessarily larger than the actual acidity (hydrogen ion concentration) of the solution.

SOLUTION

“Solution is the condition of matter which underlies and determines chemical activity. If we are ever to have a real science of chemistry we must first know the condition of matter in solution, since it is solution which gives us chemistry.”

The above statement, quoted in Jones' “New Era in Chemistry,” gives us concisely the importance of solution to the whole subject of chemistry. It is therefore essential for us to know something of the facts and theories regarding this important process and its product.

Solution, broadly speaking, consists in the dissolving of one substance, the solute, by another substance, the solvent. According to older authorities, the resulting liquid must be homogeneous, and although some have claimed that no solution is strictly homogeneous, for our present purpose we may say that homogeneity is one of the characteristics of a crystalloidal solution. To include colloidal solution in the general definition, we may think of solution as an almost infinitesimal division of the solute in the solvent, so that an effect of clearness is produced.

Solution may exist between any of the three phases of matter, but solids in liquids form by far the largest and the most important class. The solvent most generally used, as well as the one lending itself most readily to ionization, is water. Aside from water, dilute acids are the most common inorganic solvents, while benzene, alcohol and ether are the most common organic solvents.

The behavior of substances in solution, together with the reason for that behavior, has been the subject of much controversy and has led to many investigations. One of the most valuable contributions to this subject was made by Van't Hoff, who made the discovery that the laws governing the behavior of gases were also applicable to dilute solutions of a large class of substances. As previously noted, he encountered some difficulties, which led Arrhenius to give us the ionization theory, but this fact does not lessen the importance of his discovery.

Osmotic Pressure and Osmosis

The term osmotic pressure is applied to the pressure existing in a solution and is analogous to the gas pressure of a gas. It may be considered as the force which causes diffusion to take place or which causes the solute in the most concentrated part of the solution to be driven to the part with the lesser concentration. By means of semipermeable membranes, through which the water will pass, but not the solute, very accurate measurements of the osmotic pressure of various solutions have been made. The passage of the water through a so-called semipermeable membrane is known as *osmosis* and is of fundamental importance in all physiological processes of plant and animal life.

In contrast with osmosis, dialysis is the passage of crystalloids through parchment membrane. The ability to undergo dialysis is a distinguishing feature of crystalloids and is often employed as a means of separating the soluble salts from a complex fluid, like saliva. Dialysis is also important in the precipitation of colloids.

Jones' Theory of Solvation in Solution

The late Professor Harry C. Jones, of Johns Hopkins University, has suggested a very interesting and, the author believes, a very valuable theory of solution, the adoption of which removes many difficulties and explains the apparently inconsistent behavior of concentrated solutions. Briefly his theory* is as follows:—

Soluble substances form a large number of definite compounds with the solvent; the number and complexity of these hydrates diminish as the concentration of the solution increases or as the temperature rises; and for the most part the union is between the solvent and the ions, rather than the molecules, of the dissolved substance.

In other words, there seems to be general combination of the solvent and the solute—solvation in solution—one molecule of the solute uniting with a large number of molecules of the solvent. In concentrated solutions only a part of the solvent

* This theory is explained in detail in Professor Jones' book "A New Era in Chemistry," Chapter IX.

is acting as a true solvent, a considerable part having united in loose chemical combination with the solute.

Effect of Dissolved Substance on Solution

We know that if a given amount of a solid substance is added to a known volume of solution there follows a definite decrease in the freezing point of the solution and a definite increase in the boiling point. That this generalization, as well as the application of the Gas Laws referred to previously, holds true only for dilute solutions is easily explained on the basis of solvation in solution. In all concentrated solutions we have so many molecules of the solvent in combination with the molecules of the solute that the molecular concentration of the solution is obviously altered.

Effect of Variation of Solvent on Solution

In qualitative analysis we are constantly dealing with solution and we are constantly changing the reaction of the solution. The student will find it much easier to interpret the results correctly if he realizes that by changing the character of the solvent, or sometimes by merely altering its concentration or temperature, he creates entirely new conditions. For example, the sulphides of Group II only are precipitated in an acid solution, while if the solution is alkaline Group II (a), Group III and Group IV will all be precipitated out. Or again, if we take two test-tubes containing either sodium chloride or barium chloride, and to one add dilute hydrochloric acid and to the other concentrated hydrochloric acid, we shall see that, while the dilute acid has no apparent effect, the concentrated acid precipitates the salt.

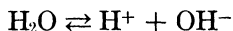
The salt is precipitated because the hydrochloric acid is much more easily soluble than the sodium chloride, and the solution becomes oversaturated with chlorine ions, causing a precipitate of the molecules of sodium chloride.

Further, in making a determination of calcium (page 158), it has been demonstrated that if the acid strength of the solution is greater than that represented by a hydrogen ion concentration of 4.0, the precipitated calcium oxalate will be dissolved, while if the acid strength of the solution becomes less than that cor-

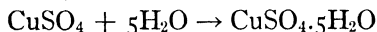
responding to a hydrogen ion concentration of 5.0, magnesium ammonium phosphate will be precipitated also.*

Hydrolysis

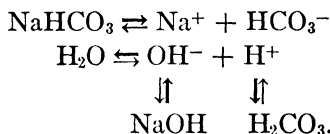
We have seen how acids, bases and salts ionize in dilute solution. That water itself ionizes to a slight extent has not been mentioned, but it is one of the fundamental facts of chemistry which must not be overlooked. Water ionizes as follows:



The fact that water ionizes gives us the phenomenon of *hydrolysis*, which is the method nature uses to a very large extent in all animal and vegetable metabolism. Hydrolysis may be defined as the utilization of the molecules of water in a chemical reaction resulting in the formation of new substances. *Hydrolysis* is to be distinguished from hydration, which is the addition of water to a compound. Thus



would be more properly called hydration, while the *basic reaction* of sodium bicarbonate, due to the formation of a trace of sodium hydroxide, is hydrolysis. This hydrolysis may be represented as follows:



Colloidal Solutions

We may consider colloidal solution as an exceedingly fine subdivision of the solute — perhaps an intermediate condition between crystalloidal solution and a mechanical suspension of a solid in a liquid. Although it is difficult to draw sharp division

* A. T. Shohl — “*P_H* and Determination of Calcium,” *Journal of Biological Chemistry*, Vol. L, No. 2, Feb., 1922.

lines between these various forms of solution, there seem to be some marked differences which serve to distinguish them.

Colloidal solutions are characterized by

- (1) Their failure to diffuse through parchment membrane
- (2) Their optical heterogeneity
- (3) The electrical energy possessed by the particles

Because a colloidal solution passes unchanged through any ordinary filter (differing in this respect from a mechanical suspension) it may cause considerable trouble in analytical work. It has been observed, however, that the presence of a strong electrolyte tends to precipitate the colloid and this fact is made use of in qualitative analysis. For example, ammonium chloride is frequently used to insure complete precipitation of such metals as nickel.

The reason for the precipitating power of the electrolyte seems to lie in the fact that colloids carry either positive or negative charges and a *negatively* charged colloid — *e.g.*, colloidal arsenious sulphide or colloidal gold — will be precipitated by the positive ion of an electrolyte. In the same way, a *positively* charged colloid, such as ferric hydroxide, will be precipitated by the *negative* ion of an electrolyte. The power of the precipitating ion has been observed to be directly proportional to its valence (Exp. 34), and if we accept the theory of valence given in the Introduction, p. 1, this is entirely reasonable.

A colloid may also be precipitated by another colloid carrying the opposite charge (precipitate of Purple of Cassius) and, as indicated above, it may be precipitated by dialysis (Exp. 33).

It has been stated that colloids carry an electric charge. There is, however, a large class of colloids, known as protective colloids, whose electric charge is very small and comparatively unimportant.

These colloids, classed by Zsigmondy as reversible, *i.e.*, colloids which upon evaporation at ordinary temperatures leave a residue soluble in water, include gelatin, albumin, gum arabic, etc. They are not affected by the presence of an electrolyte but, on the contrary, tend to keep an irreversible colloid, *i.e.*, one whose

residue upon evaporation at ordinary temperature is insoluble in water, or one carrying a decided electrical charge, in the colloidal condition. Thus, if gelatin is added to a silver nitrate solution the precipitation of silver chloride with dilute hydrochloric acid becomes impossible (Exp. 35).

CHAPTER II

QUALITATIVE ANALYSIS.

The metals, from certain physical properties, have been variously classified. Thus, in the older books, we read of the *Noble* metals, those unaffected by heat, as gold, silver, and platinum; the *Base* metals, such as iron; the *Bastard* metals, those easily crystallizable, as antimony and zinc; the *Metalloids*, sodium and potassium.

As it became better understood that the properties of metals were to a considerable extent dependent upon conditions of temperature and pressure, other classifications came to be used. We may group metals according to the chemical behavior of their salts, irrespective of their properties as metals. Thus, Ag, Pb, and Hg (mercurous) form a group of metals whose chlorides are insoluble in water or dilute acids. These metals may consequently be thrown out of solution or precipitated by the addition of HCl to any solution of their salts. We therefore let Ag, Hg', and Pb constitute the *First Analytical Group*, and HCl is the *First Group Reagent*.

In like manner, we find a group of nine metals that are precipitated from dilute acid solution by hydrosulphuric acid (H_2S). These metals are Cu, Cd, Bi, Hg'', As, Sb, Sn, Au, and Pt, and constitute the *Second Analytical Group*, while H_2S is the *Second Group Reagent*.

The fact that the sulphides formed by the first four of these metals are *insoluble* in ammonium sulphide, and those formed by the last five are soluble, furnishes a simple method of separating this group into two parts, *a* and *b*:

Pb,* Cu, Cd, Bi, and Hg'' constitute Group II (*a*) and As, Sb, Sn, Au, and Pt, Group II (*b*).

* Lead is included in this group because it is not entirely separated as a chloride in Group I, traces of it remaining in solution even after addition of HCl.

Thus, the metals are divided into various analytical groups, each with its own peculiar group reagent.

The precipitates produced by these various group reagents have their individual peculiarities of solubility, which must be carefully studied and considered during the process of analysis. Three conditions are particularly to be noted: the acid strength of the solution, the character of the solvent, and the temperature. (See laboratory experiments on page 173.) Different groupings are possible, and hardly any two analysts will employ exactly the same scheme for identifying all the metals, although the following group divisions are generally used:

Analytical Groups.

Group I. — Ag, Pb, and Hg'. Metals that form insoluble chlorides and are precipitated from aqueous solution by HCl (the group reagent).

Group II (a). — Cu, Cd, Bi, Hg'', and Pb. Metals that form sulphides insoluble in dilute HCl solution and also insoluble in ammonium sulphide.

Group II (b). — As, Sb, Sn, Au, and Pt. Metals that form sulphides insoluble in dilute HCl but soluble in yellow ammonium sulphide, or alkaline hydrates.

Group III. — Fe, Al, and Cr. In solutions free from H₂S and which do not contain phosphates, oxalates, tartrates, or salts of certain other organic acids, these three metals may be separated by ammonium hydrate (NH₄OH).

Group IV. — Co, Ni, Mn, and Zn. Metals forming sulphides soluble in acid but insoluble in alkaline solution. Ammonium sulphide, (NH₄)₂S, is the group reagent.

Group V. — Ba, Sr, Ca and Mg.* Metals forming carbonates, insoluble in alkaline solutions. The group reagent is ammonium carbonate, (NH₄)₂CO₃.

Group VI. — K, Na, Li, NH₄. Metals which cannot be pre-

* In the process of analysis, magnesium is held in solution by the presence of NH₄Cl and is not thrown out as a carbonate with the other three members of the group.

precipitated by any single reagent and for which it is necessary to make individual tests.

It is our purpose to take up the study of the metals according to their analytical grouping: first, the deportment of their salts in solution; later, the metals themselves and their specific application to dentistry.

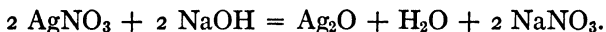
SALTS OF GROUP I METALS

The metals separated in this group are silver, lead, and mercurous mercury, the salts of which will be briefly considered.

SILVER

Salts of silver are liable to decomposition by the action of light, with reduction in greater or less degree to metallic silver. The salts change from violet to black, according to the amount of silver reduced. Such reduction is illustrated in the use of the ordinary photographic plates and paper.

Silver oxide (Ag_2O), a dark brown powder, may be produced in the wet way, i.e., by precipitation of soluble silver salts with hydroxides of the fixed alkalis.



Silver hydroxide (white) may be formed if the above reaction is brought about in alcoholic solution; but it is a very unstable compound, quickly changing to $\text{Ag}_2\text{O} + \text{H}_2\text{O}$. Silver thiosulphate, $\text{Ag}_2\text{S}_2\text{O}_3$, may be precipitated white from solution of silver nitrate and sodium thiosulphate. Excess of the thiosulphate produces a soluble double salt, NaAgS_2O_3 . This fact may be utilized in the removal of silver stains.

Fused silver nitrate, in the form of pencils or small sticks, is used as an escharotic, and is known as "lunar caustic." Dilute lunar caustic consists of equal parts of AgNO_3 and KNO_3 fused together in pencil form.

Analytical Reactions. — Make the following tests with a weak solution of AgNO_3 (about 2 per cent). Write the reactions and enter color and solubility of each precipitate formed in laboratory note-book.

AgNO_3 with HCl gives a white curdy precipitate of AgCl which darkens by action of sunlight. If Ag solution is very dilute the precipitate will assume the curdy appearance and filter more easily if it is heated and rotated quite rapidly in the test-tube. Allow the precipitate to settle. Decant the liquid carefully, divide precipitate into two parts, and test its solubility in dilute nitric acid, also in ammonia water.

AgNO_3 with KBr gives a white precipitate of AgBr , less easily soluble in ammonia than the AgCl .

AgNO_3 with KI gives a pale yellow precipitate of AgI , insoluble in ammonia.

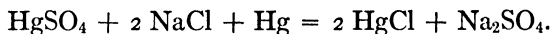
AgNO_3 with H_2S gives a black precipitate of Ag_2S . AgNO_3 with K_2CrO_4 gives a red precipitate of Ag_2CrO_4 in neutral solution. Test the solubility of Ag_2CrO_4 in NH_4OH , HCl , and HNO_3 .

MERCURY

Mercury forms two series of salts; one, mercurous, referable to the oxide Hg_2O , in which mercury exhibits a valence of one; and the other, mercuric, referable to HgO , the mercury having a valence of two.

(Mercuric compounds will be considered under group two.)

Mercurous chloride, or calomel, may be made by the reduction of HgCl_2 by a reducing agent, as SO_2 . $2 \text{HgCl}_2 + 2 \text{H}_2\text{O} + \text{SO}_2 = 2 \text{HgCl} + \text{H}_2\text{SO}_4 + 2 \text{HCl}$; but the method usually employed in the commercial preparation of calomel is to sublime a mixture of mercuric sulphate, sodium chloride and mercury.



Mercurous iodide, HgI , is a greenish, unstable salt produced by double decomposition of HgNO_3 and KI .

Mercurous nitrate is an easily soluble salt, produced by action of cold nitric acid on excess of mercury, a solution of which may be used for the study of mercurous precipitates.

Note. — The solution of mercurous nitrate, upon standing, will be found to contain more or less mercuric nitrate, unless care is taken to keep excess of mercury in the bottom of the bottle.

Analytical Reactions. — HgNO_3 with HCl gives a white precipitate of HgCl (calomel). After the precipitate has settled, decant the liquid, and test the solubility of the HgCl in ammonia water. Does it dissolve? How does its behavior differ from that of AgCl ?

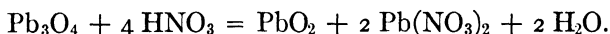
Alkaline hydroxides form, with mercurous salts, the black oxide Hg_2O , a preparation of which, made with lime-water and calomel, is known as "black wash."

LEAD

Lead forms five oxides, three of which are of analytical interest.

Litharge, PbO , is the yellow oxide used in pharmacy as the base of "diachylon plaster."

The black oxide, PbO_2 , is used as an oxidizing agent. Red lead (minium), Pb_3O_4 , is practically a mixture of PbO_2 and 2 PbO , and is used as a source of PbO_2 which is obtained by treatment with HNO_3 .



Lead carbonate, as prepared by precipitation of soluble lead salts by alkali carbonates, has the composition $(\text{PbCO}_3)_2\text{Pb}(\text{OH})_2$.

The basic carbonate, prepared by exposure of the metal to fumes of acetic acid, CO_2 , and moisture, is known as "white lead," and is used in the manufacture of paint.

Lead acetate, or sugar of lead, formed by solution of the metal or the oxide, PbO , in acetic acid, is a white soluble salt crystallizing with three molecules of H_2O . The solution has an acid reaction to litmus paper.

Lead subacetate, or basic acetate of lead, a solution of which is known as Goulard's extract,* is made by boiling lead acetate solution with litharge. It is used in medicine as an external application and in physiological chemistry as a reagent. It deteriorates by absorption of CO_2 and precipitation of a carbonate.

Lead chromate (chrome yellow) is a yellow, insoluble salt used as a pigment.

* Preparation in Appendix Vol. II.

Lead nitrate, an easily soluble, white, crystalline salt, may be used in the study of the analytical reactions of lead.

Lead arsenate, a poisonous salt, is quite largely used for spraying trees.

Analytical Reactions. — $\text{Pb}(\text{NO}_3)_2$ with 2 HCl gives white precipitate of PbCl_2 . Test its solubility in hot water and in NH_4OH .

$\text{Pb}(\text{NO}_3)_2$ with NH_4OH gives white precipitate of $\text{Pb}(\text{OH})_2$, insoluble in hot water.

$\text{Pb}(\text{NO}_3)_2$ with H_2S gives black PbS . Test solubility of precipitate in warm dilute HNO_3 .

$\text{Pb}(\text{NO}_3)_2$ with H_2SO_4 gives white precipitate of PbSO_4 , forming slowly in dilute solutions.

$\text{Pb}(\text{NO}_3)_2$ with K_2CrO_4 (or $\text{K}_2\text{Cr}_2\text{O}_7$) gives a yellow precipitate of PbCrO_4 .

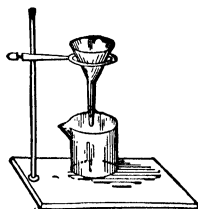
$\text{Pb}(\text{NO}_3)_2$ with KI gives a yellow precipitate, PbI_2 . Avoid excess of the potassium iodide.

By application of the reactions of the salts of Ag , Pb , and Hg' , we may formulate a scheme for the separation and identification of the metals of Group I, as follows:

Analysis of Group 1.

(Ag , Pb , Hg' .)

To the clear solution to be tested, slowly add dilute HCl as long as any precipitation occurs. Filter and wash the precipitate *once* with cold water, add this washing to filtrate to be tested for remaining groups, then wash precipitate on the paper with several small portions of *hot* water.



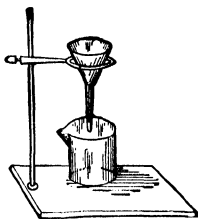
AgCl and HgCl remain undissolved.

PbCl_2 is in the hot-water solution.

Divide this hot-water solution into three parts and make three of the following tests for lead: *First*, with $\text{K}_2\text{Cr}_2\text{O}_7$, which

gives yellow precipitate of PbCrO_4 . *Second*, with dilute H_2SO_4 , giving a white precipitate of PbSO_4 . *Third*, with H_2S water, giving black precipitate of PbS . *Fourth*, with KI solution, which forms a yellow precipitate of PbI_2 . Write these reactions.

To undissolved residues of Hg and Ag chlorides, add warm NH_4OH .



Hg remains on the paper, black, as $\text{Hg} + \text{NH}_2\text{HgCl}$.

Ag is dissolved by the NH_4OH and may be precipitated as AgCl by adding HNO_3 to acid reaction. Presence of Hg in the black residue may be confirmed as in Group II (page 40).

OUTLINE SCHEME FOR ANALYSIS OF GROUP I.

To about one-third of a test-tubeful of the unknown solution, add a few drops of HCl .

Ppt. = AgCl , HgCl , PbCl_2 . Filter, add hot H_2O .

Residue = AgCl , HgCl . Add NH_4OH .		Solution = PbCl_2 . Test as on page 25.
Residue = $\text{Hg} + \text{NH}_2\text{HgCl}$. Test, as above.	Solution = $\text{Ag}(\text{NH}_3)_2\text{Cl}$. Test with HNO_3 .	

QUESTIONS ON GROUP I.

Why wash the precipitated chlorides only *once* with cold water?

Why is it necessary to wash the lead chloride out with hot water before using ammonia?

Why is ammonia used?

How does nitric acid reprecipitate silver chloride?

Why is it necessary to use two or more confirmatory tests for the presence of lead?

What other metal in group I would give a black precipitate with hydrogen sulphide water?

What precaution must be used in testing for soluble salts of lead with potassium iodide?

SALTS OF GROUP II METALS

COPPER

Salts and solutions of copper are usually blue or green. Copper forms two series of salts: the cuprous, of which there are but few important examples, and the cupric. Cuprous oxide, Cu_2O , which is red in color (sometimes yellow through admixture of cuprous hydroxide) is obtained by reduction of cupric salts by organic substances, such as sugar. Cuprous chloride is used as a reagent for the detection of acetylene gas. Cuprous iodide is a white, insoluble powder used in the preparation of the white copper cements. (See page 136.)

Cupric oxide, CuO , is a black powder formed by ignition of copper in the air, or by boiling copper solution with the fixed alkali hydroxides.

Copper arsenate and aceto-arsenite, the latter known as Paris green, are both green powders which have been used as pigments and as insecticides.

Copper sulphate, CuSO_4 , crystallizes with five molecules of water and is known as bluestone or blue vitriol. It is used extensively in the "gravity battery," and in copper plating.

Verdigris is a subacetate or oxyacetate of copper; composition $\text{Cu}_2\text{O}(\text{C}_2\text{H}_3\text{O}_2)_2$.

Copper salts combine with ammonia, forming a series of "cuprammonium" compounds, freely soluble and of intense blue color.

The chloride, nitrate and sulphate are the common soluble salts. A 1 per cent solution of either of these will give the analytical reactions.

Analytical Reactions. — CuSO_4 with H_2S gives CuS , a brownish black sulphide. Test its solubility in $(\text{NH}_4)_2\text{S}$ and in warm dilute HNO_3 .

CuSO_4 with NH_4OH (one or two drops of reagent) will precipitate $\text{Cu}(\text{OH})_2$, bluish white. Add more NH_4OH to the same test-tube and note the result. To this clear solution add a sufficient amount of dry KCN to completely decolorize the liquid. Then add to the mixture some H_2S water. Is the black CuS

thrown out? The behavior of Cu solutions thus treated is due to the formation of double salts, the solution in ammonia being due to a compound of CuSO_4 and NH_3 , and the decolorization of the blue solution to one of $\text{Cu}(\text{CN})_2$ and KCN .

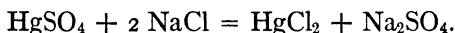
CuSO_4 with $\text{K}_4\text{Fe}(\text{CN})_6$ (potassium ferrocyanide) gives, in acetic acid solution, a red-brown precipitate of $\text{Cu}_2\text{Fe}(\text{CN})_6$.

MERCURIC MERCURY.

Mercuric oxide, HgO , is a red powder obtained by ignition of mercury in the air. Mercuric oxide may also be prepared by precipitation of mercuric chloride with alkaline hydroxides. The oxide thus formed is yellow in color, and, when prepared by mixing mercuric chloride and lime water, forms the "yellow wash" used to a considerable extent in pharmacy.

Mercuric chloride, HgCl_2 , is an intensely poisonous salt, known by the fairly descriptive name of corrosive sublimate. It corrodes metals, such as zinc and iron; it coagulates albumin and acts as a corrosive poison when taken internally.

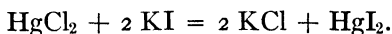
It is made in a manner analogous to that used for the preparation of calomel, i.e., by sublimation, the salts used in this instance being mercuric sulphate and sodium chloride alone.



Mercuric chloride is antiseptic and is used as a disinfectant in dilutions of one to a thousand. Antiseptic tablets, designed to give about this strength of solution by the addition of one tablet to one pint of water, are made to contain 7.7 grains HgCl_2 , and 7.3 grains NH_4Cl , with sufficient purple coloring to advertise the nature of the tablets and thus act as a safeguard against accidental poisoning. Mercuric chloride is soluble in water and in alcohol. It is used in the preparation of antiseptic gauze, sterile cotton, etc., but, on account of its corrosive properties, cannot be used to sterilize instruments.

Ammoniated mercury, mercur-ammonium chloride, or white precipitate, (NH_2HgCl) is a white powder obtained by slowly pouring a solution of HgCl_2 into ammonia water.

Mercuric iodide, red iodide (HgI_2), is made by reaction of mercuric chloride with potassium iodide:



Mercuric iodide is soluble in excess of either reagent, also in alcohol.

Mercuric iodide combines with potassium iodide (KI), forming an iodo-hydrargyrate, used as a reagent in physiological chemistry, also as an alkaloidal precipitant.

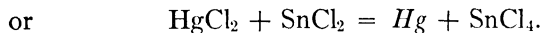
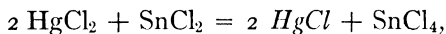
An alkaline solution of potassium iodo-hydrargyrate constitutes Nessler's reagent, used in analysis of water and of saliva as a test for ammonium compounds.

Analytical Reactions. — A 2 per cent solution of corrosive sublimate (HgCl_2) may be used in demonstrating the reactions of dyad mercury.

HgCl_2 with H_2S gives first a white precipitate, turning yellow, brown, and finally black, as the proportion of H_2S increases. The black precipitate *only* is mercuric sulphide, and care must be taken to add H_2S till this compound is produced.

Test the solubility of HgS in $(\text{NH}_4)_2\text{S}$ and HNO_3 .

To HgCl_2 solution add SnCl_2 . The mercuric chloride is reduced to mercurous chloride (HgCl , white) or metallic mercury (Hg , gray), according to proportions used:



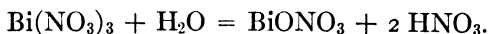
HgCl_2 with KI gives red HgI_2 , easily soluble in excess of either of the reagents.

HgCl_2 with NH_4OH gives white precipitate of $(\text{NH}_2\text{Hg})\text{Cl}$, known as "white precipitate" (see ammoniated mercury). "Red precipitate" is a term sometimes used to designate the red oxide of mercury, HgO , made in the dry way.

BISMUTH

Salts of bismuth, as a rule, require excess of acid for permanent solution; and, by adding a considerable volume of water they are

easily thrown out of solution as insoluble basic or oxysalts, the reaction of the nitrate being as follows:



This may be demonstrated by allowing a few drops of bismuth solution to fall into a comparatively large amount of water (two to six ounces). A white cloud of insoluble oxysalt may be observed settling through clear water. This may be employed as a final test for bismuth in the course of systematic analysis.

The subnitrate and the subcarbonate of bismuth are both used in medicine. The latter is a common starting-point in the preparation of other bismuth salts.

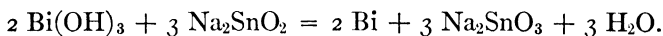
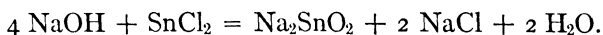
Analytical Reactions. — The most available salt is the nitrate, insoluble in water unless strongly acidulated.

Use a 2 per cent solution of $\text{Bi}(\text{NO}_3)_3$ in the following tests:

$\text{Bi}(\text{NO}_3)_3$ with NH_4OH gives white precipitate of bismuth hydroxide $\text{Bi}(\text{OH})_3$.

$\text{Bi}(\text{NO}_3)_3$ with H_2S precipitates Bi_2S_3 , brownish-black, insoluble in $(\text{NH}_4)_2\text{S}$, but soluble in warm dilute HNO_3 .

$\text{Bi}(\text{OH})_3$ reacts with sodium stannite (prepared by adding NaOH to SnCl_2 till precipitate dissolves) giving a black precipitate of metallic bismuth.



CADMIUM.

Cadmium salts are generally white. The sulphate and nitrate are common, and a 2 per cent solution of either may be used in studying the following reactions.

Analytical Reactions. — CdSO_4 with H_2S gives a bright yellow sulphide, CdS , soluble in dilute nitric acid.

CdSO_4 with $(\text{NH}_4)_2\text{S}$ also precipitates the yellow sulphide.

Cadmium sulphide forms slowly, and, in presence of Cu or other second-group metals, may escape precipitation if the reagent is added in insufficient quantity.

Cadmium hydroxide is white, soluble in NH_4OH . Cadmium

iodide is a white salt, soluble in alcohol and water and with potassium iodide is used as an alkaloidal precipitant known as Marmé's reagent.

ARSENIC.

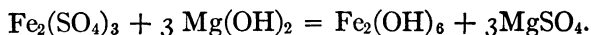
Arsenic forms two series of salts, the arsenious, As^{III} , and the arsenic, As^{V} , and it also acts as an acid radical forming arsenious and arsenic acids. In the process of analysis, arsenic compounds, whether acid or basic, are reduced to arsenious by action of hydrogen sulphide. It is most easily obtained in the form of the trioxide, As_2O_3 , also known as arsenious acid or white arsenic.

White arsenic is intensely poisonous; nevertheless, it has been very freely used in curing the skin of fur-bearing animals and otherwise as a preservative. In dentistry, white arsenic is used to devitalize pulp.

Arsenic is widely distributed in nature. It occurs in soft coal, from which source it finds its way into the roadside dust and any substance capable of holding dust, such as the majority of fabrics, wall papers, etc. Arsenic is a common impurity in mercury, zinc, and commercial acids. Inasmuch as these things are largely used in the preparation of amalgam and cement fillings, it is necessary that considerable pains be taken to prevent the presence of the poison in sufficient quantity to cause irritation.

The poisonous character of arsenic differs greatly with the combination in which it occurs. A gaseous hydride of arsenic, AsH_3 , is among the most poisonous of its compounds, while some of the organic compounds are claimed to be non-poisonous.

Arsenic forms an insoluble arsenate with ferric hydrate; hence, freshly precipitated ferric hydroxide is the official antidote for arsenical poisoning. This is prepared by mixing 150 c.c. of dilute ferric sulphate solution (containing 50 c.c. of the U.S.P. "Solution") with a well-shaken mixture of 10 grains of oxide of magnesium in about 750 c.c. of water:



The following are Pharmacopœial preparations of arsenic: Fowler's solution, containing 1 per cent As_2O_3 dissolved by use of potassium bicarbonate; a solution of arsenious acid, containing

1 per cent As_2O_3 dissolved by the aid of two parts of HCl ; Donovan's solution, containing 1 per cent each of AsI_3 and HgI_2 ; and Pearson's solution, containing 1 per cent sodium arsenate.

Analytical Reactions. — A solution for studying the reactions of arsenic (As^{III}) is conveniently made by dissolving about 15 grams of white arsenic in dilute NaOH solution by the aid of heat, then diluting to one liter and acidifying slightly with HCl .

To an arsenious solution, which may be represented by AsCl_3 , add H_2S water. A lemon-yellow precipitate of As_2S_3 will be thrown down. Test the solubility of this precipitate in yellow ammonium sulphide and in ammonium carbonate.

To the alkaline solution of the sulphide, add excess of HCl ; As_2S_3 is precipitated.

To an arsenious solution add $(\text{NH}_4)_2\text{S}$ in repeated small portions.

In neutral solution, as of sodium arsenite, Na_3AsO_3 , silver nitrate will throw down yellow silver arsenite, soluble in excess of nitric acid or ammonia.

SPECIAL TESTS FOR ARSENIC.

REINSCH'S TEST for arsenic, applicable to any solution whether organic or not, and very valuable as a preliminary test, is made as follows: Place the solution or mixture to be tested in a porce-



FIG. 1.

lain dish, acidify strongly with hydrochloric acid, add a small strip of bright copper foil (cleaned in dilute nitric acid and thoroughly washed in distilled water) and boil for ten or twenty minutes, adding sufficient water to replace loss by evaporation. Remove the copper foil; a dark gray to black coating is an indication of arsenic but is not conclusive, as some other substances, mercury and antimony in particular, give similar deposits.

To prove the presence of arsenic, roll the foil as tightly as possible and place it in the bulb of a small glass matrass (Fig. 1).

Heat the bulb over a very small luminous flame, when tetrahedral or octahedral crystals of arsenious trioxide (As_2O_3) will

deposit in the constricted portion of the tube. These may be identified by microscopical examination. There will be sufficient air in the matrass for the formation of the oxide. Thus the test becomes much more delicate than if the foil were heated in the ordinary open tube as often recommended.

GUTZEIT'S TEST is made by placing the suspected solution in a test-tube, acidifying with sulphuric acid, adding a few small pieces of arsenic-free zinc, and, as hydrogen begins to be given off, placing over the mouth of the tube a piece of filter-paper carrying a drop of a strong solution of silver nitrate. The presence of arsenic is indicated by the darkening of the moistened filter-paper in accordance with the following reactions:

The nascent hydrogen, liberated by action of the zinc upon the acid, forms, with any arsenic present, the gaseous arsenious hydride which, in contact with the filter-paper wet with silver nitrate solution, produces a brown or black stain of metallic silver, while the arsenic becomes arsenious acid, H_3AsO_3 . The stain may possibly be yellow, by formation of a compound of silver *arsenide* and silver nitrate, but, as a rule, moisture is present in sufficient amount to insure the decomposition of this compound.

Antimony will give a similar brown or black stain (not yellow), but the presence of arsenic may be conclusively demonstrated by making FLEITMANN'S TEST, which is conducted in the same way as the preceding, except that the hydrogen is evolved in alkaline solution, either by means of zinc and strong potassium hydroxide solution ($\text{Zn} + 2\text{KOH} = \text{K}_2\text{ZnO}_2 + \text{H}_2$) or by sodium amalgam (made with arsenic-free mercury) and water ($\text{NaHg}_x + \text{H}_2\text{O} = \text{NaOH} + \text{Hg} + \text{H}$). In this case the antimony hydride is *not formed*; so a stain thus obtained constitutes a positive test for *arsenic*.

MARSH'S TEST for arsenic (or antimony) consists of a simple hydrogen generator with glass tip for burning the gas, as shown in Fig. 2. In this apparatus, antimony and arsenic are converted into the gaseous

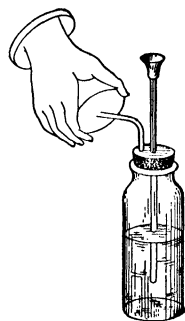


FIG. 2.

hydrides, arsenic hydride, and antimony hydride; and if a piece of cold porcelain is pressed down upon the flame, arsenic or antimony will be deposited as metallic stains (mirrors) upon the porcelain.

Traces of antimony may be retained in the generator by the introduction of a piece of platinum foil, the antimony being precipitated upon the platinum, to which it adheres quite strongly.

To distinguish between arsenic and antimony spots, the following tests will suffice:

Arsenic.

Brown-black, lustrous spots.
Soluble in solution of hypochlorite of lime or soda.
Easily volatilized.

Antimony.

Dead brown or black surfaces.
Insoluble in solution of hypochlorite of lime or soda.
Volatilized at red heat.

The MARSH-BERZELIUS TEST for arsenic is the most delicate of all and the one to which we resort in detecting arsenic in

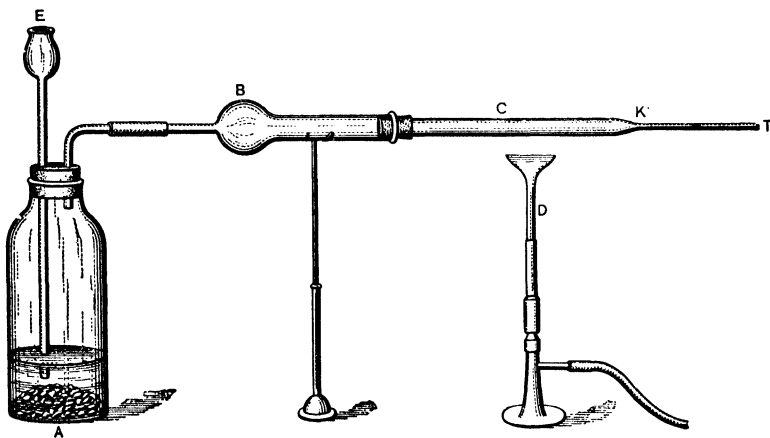


FIG. 3.

the saliva or the urine. By this method $1/200$ of a milligram, or about $1/12800$ of a grain, can be easily shown as a brown deposit in the constricted tube at about the point *K*, Fig. 3. The apparatus used in this test is shown in Fig. 3, and consists of a small Erlenmeyer flask, or wide-mouth bottle, fitted as a hydrogen generator, *A*, and connected with a drying-tube, *B*,

filled with fused calcium chloride, then with a tube of hard glass, *C*, drawn out to a very small diameter for half its length.

The generator *A* is charged with arsenic-free zinc, and dilute sulphuric acid (1/5) introduced through the thistle-tube *E*. After all air has been driven from the apparatus, light the escaping hydrogen at *T*, then the Bunsen burner *D*, and allow the generator to run for about twenty minutes, thus making a blank test of apparatus and reagents. If at the end of this time the hard glass is perfectly free from any deposit, the suspected liquid, which must have been freed from organic matter (process described in detail in chapter on Urine Analysis, Vol. II), may be introduced in portions of about 10 c.c. each.

The flame should be spread somewhat, so as to heat at least 1 inch of the glass tube. This may be accomplished, in the absence of a burner-tip, by placing an inverted V-shaped piece of asbestos board, one inch wide, over the heated part of the tube.

The presence of arsenic increases the evolution of hydrogen, and, unless the solution is added gradually, the arsenious hydride may be driven so rapidly past the flame as to escape decomposition, or the tube may become heated to such an extent that arsenic will not be deposited.

The escape of arsenic at *T* may be noticed by the bluish color of the flame and by the characteristic garlic odor.

Antimony is similarly deposited as a stain, which in this case is dead-black instead of brown-black; and as antimony is less easily volatilized than arsenic the deposit will be nearer the flame, possibly on both sides of it.

MERCURIC BROMIDE TEST. — Sanger and Black* have modified the Gutzeit test, making the determination of arsenic a

* Proceedings of the American Academy of Arts and Sciences, Vol. XLIII, No. 8, October 1907.

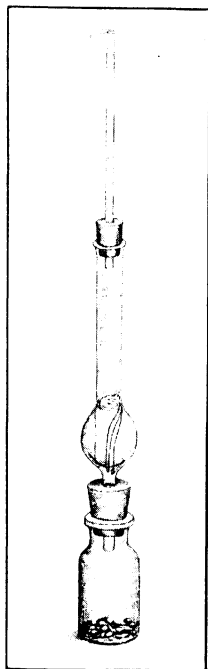


FIG. 4.

quantitative one, as follows: The arsenious hydride is passed through a drying tube containing filter-paper (in bulb, Fig. 4) **wet** with lead acetate solution to absorb sulphur compounds. Then the gas is passed through absorbent cotton in the upper part of the drying tube, and then over a paper moistened with mercuric chloride (small tube above drying tube) when the arsenic produces a yellow to brown color on the strip of filter-paper.

The delicacy of this test may be increased by using mercuric bromide in place of mercuric chloride. An advantage of this process is that it is carried on without the application of heat and consequently without the danger of exploding any mixture of hydrogen and air. The HgBr_2 paper is stained yellow to brown, beginning at the end next to the generator, and if conditions are carefully regulated the extent of the stain may have a quantitative value.

Arsenic compounds (As^v), as Na_2HAsO_4 , are of but little interest from the dentist's standpoint.

All arsenic compounds are reduced by nascent hydrogen to arsenious combinations, then to elementary arsenic, then to arsine, (AsH_3); hence, the special tests given for arsenious compounds are applicable.

Free chlorine, nitric acid, and potassium ferricyanide oxidize arsenious compounds to arsenic; in this condition the arsenic is not easily volatilized, and organic matter may be destroyed by deflagration (in presence of excess of nitrates) with but slight loss of arsenic.

ANTIMONY.

The salts of antimony may be classified as antimony salts, referable to the hydroxide $\text{Sb}(\text{OH})_3$, and antimonyl salts, referable to $\text{SbO}(\text{OH})$.

Butter of antimony, antimony trichloride, SbCl_3 , when pure, is a colorless solid of buttery consistency, hence its name. It may be formed by direct union of constituent elements.

Salts of antimony tend to form oxycompounds and are held in solution by excess of acid. The antimonious chloride SbCl_3 , in solution with hydrochloric acid, is precipitated by excess of water, as a white oxychloride $\text{Sb}_4\text{Cl}_2\text{O}_5$, also known as "powder

of Algaroth.” The antimonie chloride in like manner precipitates the antimonie oxychloride, SbOCl_3 . Demonstrate by turning 1 or 2 c.c. of SbCl_3 solution into a large excess of water.

Tartar emetic, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$, may be prepared by boiling antimony oxide and bitartrate of potassium, filtering and allowing the hot solution to crystallize. It crystallizes with one-half molecule of water.

Analytical Reactions. — A 2 per cent aqueous solution of tartar emetic may be used in the following tests:

To an antimony solution represented by SbCl_3 add H_2S water: Sb_2S_3 is precipitated, orange-red. Test solubility of the precipitate in $(\text{NH}_4)_2\text{S}$ and in $(\text{NH}_4)_2\text{CO}_3$.

How does it differ from arsenic?

Upon the addition of HCl in excess to the ammonium sulphide solution, the Sb is reprecipitated, not necessarily as Sb_2S_3 , but more usually as Sb_2S_5 or a mixture of the two sulphides.

TIN.

The salts of tin are not used in medicine but are useful as laboratory reagents.

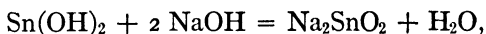
The chloride (SnCl_2), prepared as suggested under properties of the metal, is used in solution as a test for mercury.

The stannic salts are the more stable, and this solution of stannous chloride easily becomes stannic chloride unless excess of metallic tin is kept in the solution.

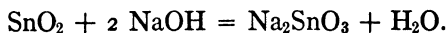
Stannous nitrate may be produced by the action of cold nitric acid as follows:



Tin may act as an acid-forming element in such compounds as sodium stannite (Na_2SnO_2), produced by the solution of stannous hydrate in sodium hydrate,



or sodium stannate, produced when stannic oxide is fused with sodium hydrate,



Metallic zinc thrown into a tin solution will precipitate the tin as follows: $\text{SnCl}_2 + \text{Zn} = \text{ZnCl}_2 + \text{Sn}$.

This reaction is used in the separation of tin from antimony in the second group. Here in order to obtain the tin in soluble form suitable for a final test, it is first necessary to add sufficient hydrochloric acid to dissolve *all* the zinc present as otherwise the tin may adhere to it.

Tin, like arsenic and antimony, forms two series of salts, the stannous (Sn^{II}) and the stannic (Sn^{IV}). A little HCl treated with excess of granulated tin till hydrogen is no longer given off furnishes a solution of stannous chloride suitable for the following experiments:

Analytical Reactions. — SnCl_2 with H_2S gives brown precipitate of SnS , soluble in $(\text{NH}_4)_2\text{S}$, insoluble in $(\text{NH}_4)_2\text{CO}_3$.

SnCl_2 with HgCl_2 gives a white or gray precipitate, as explained on page 29 under "Mercury," and is used as a test for the presence of mercury. It may also be used as an alkaloidal precipitant.

Strong solutions of SnCl_2 in presence of metallic Sn keep fairly well, but dilute solutions without an excess of tin oxidize very rapidly to stannic combinations and cease to be of value as reagents.

GOLD

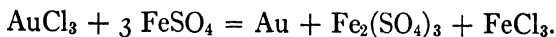
Common soluble salts of gold are the chloride, AuCl_3 , and the so-called gold and sodium chloride, which is more accurately a sodium chloraurate, NaAuCl_4 , a salt of chlorauric acid.

Analytical Reactions. — A one-half per cent solution of AuCl_3 may be used in the following tests:

H_2S with AuCl_3 gives dark brown Au_2S_3 (auric sulphide), soluble in yellow ammonium sulphide.

Gold is reduced to the metallic state by many of the other metals, as Pb, Cu, Ag, Sn, Al, Sb, Fe, Mg, Zn, and Hg; also by ferrous sulphate, stannous chloride, and oxalic acid.

Add a freshly prepared solution of ferrous sulphate to a little acid solution of AuCl_3 . Gold is precipitated as follows:



Stannous chloride precipitates from gold solution the "purple of Cassius," consisting of a mixture of gold and oxide of tin in colloidal forms.

Gold is slowly precipitated by oxalic acid; $2 \text{AuCl}_3 + 3 \text{H}_2\text{C}_2\text{O}_4 = 6 \text{HCl} + 6 \text{CO}_2 + 2 \text{Au}$; as Pt is not precipitated at all by this reagent, it is possible to separate Au and Pt in solution of the chlorides, by this means.

KI will give a dark-green precipitate of AuI_2 , provided the KI is in excess; if the gold is in excess, the precipitate is apt to be the yellow AuI (aurous iodide). In the presence of a considerable excess of KI the AuI_3 is kept in solution as the potassio-auric iodide, KIAuI_3 . The reduction of this double salt by sodium thiosulphate is made the basis of the method to determine the quantity of Au in a given alloy, as described in the chapter on Volumetric Analysis.

PLATINUM

Platinum with aqua regia forms platinum chloride and, like gold, gives a soluble double salt with sodium, sodium chlorplatinate, Na_2PtCl_6 , referable to chlorplatinic acid. The corresponding potassium and ammonium salts of chlorplatinic acid are yellow crystalline compounds (Plate I, Figs. 2 and 4) and, being only slightly soluble in water and insoluble in alcohol, furnish a method for the separation of the alkali metals.

Both of these double insoluble salts are soluble in excess of alkali, and reprecipitated by HCl.

Analytical Reactions. — $\text{PtCl}_4 + \text{H}_2\text{S}$ gives an almost black precipitate of sulphide of platinum, soluble in yellow ammonium sulphide.

Stannous chloride reduces PtCl_4 to PtCl_2 but forms no precipitate. Metallic Zn will precipitate platinum as a fine black powder or spongy mass.

Oxalic acid does not precipitate platinum.

Analysis of Group II.

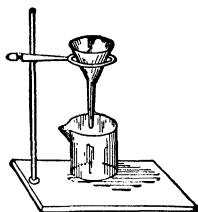
Separation of parts (a) and (b)

A portion of the clear filtrate, from Group I, containing a slight excess of HCl , is tested for metals of Group II by the addition of H_2S water.*

If a precipitate is obtained, warm the *whole* of the solution and pass in H_2S gas for three to five minutes, thus precipitating all metals of the group as sulphides. Filter.

Break point of filter-paper with glass rod and wash Group II into beaker with warm $(\text{NH}_4)_2\text{S}$; digest hot for a few minutes.

Filter and wash the precipitate till wash-water shows only traces of Cl . Throw away all wash-water except the first.

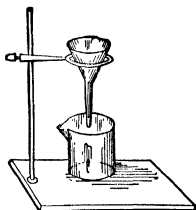


Group II (a). Cu , Cd , Bi , Hg , and Pb .

Group II (b). As , Sb , Sn , Au , and Pt .

Analysis of Group II(a).

Dissolve the precipitate off the paper with hot dilute HNO_3 .



Hg , if present, will remain on paper, black.

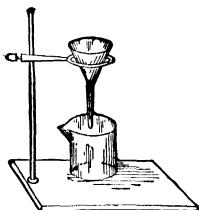
Filtrate contains nitrates of Pb , Cu , Cd , and Bi .

Test black residue on paper for Hg^{II} by dissolving in aqua regia and precipitating with SnCl_2 . For reaction between SnCl_2 and HgCl_2 , see page 29. Aqua regia may be made by mixing two or three parts of HCl with one part of HNO_3 . Free Cl is liberated and dissolves the HgS as HgCl_2 .

* A preliminary test is made on a part of the solution because, in the absence of Group II, the analysis of Group III can be made more easily without the presence of H_2S .



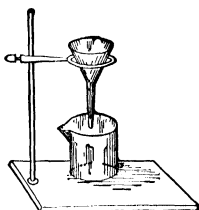
If lead is present in Group I, the above filtrate will contain traces which must be separated by the addition of a few drops of H_2SO_4 and allowing to stand at least fifteen minutes. Filter.



PbSO_4 remains on paper.

Filtrate contains Cu, Cd, Bi.

To the filtrate add NH_4OH till alkaline; Bi separates as $\text{Bi}(\text{OH})_3$, white. Filter. Confirmatory test for bismuth may be made by pouring over the precipitated $\text{Bi}(\text{OH})_3$ on the paper a solution of sodium stannite. If bismuth is present the precipitate turns black in accordance with the reaction given on page 30.



$\text{Bi}(\text{OH})_3$.

Cu and Cd.

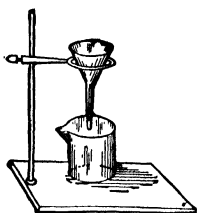
Divide the filtrate (Cu and Cd) into two parts. A blue color indicates presence of Cu. With one part, test for Cu by making it acid with acetic acid and adding $\text{K}_4\text{Fe}(\text{CN})_6$, which will give a brown precipitate of $\text{Cu}_2\text{Fe}(\text{CN})_6$. With the other part, test for Cd by adding solid KCN very carefully till all blue color has disappeared; then a little H_2S water will give a yellow precipitate of CdS if cadmium is present.

Analysis of Group II (b).

To the ammonium sulphide solution, add HCl till acid. A very fine white precipitate may be sulphur only.

Filter and wash. Throw away wash-water. Pierce paper

and wash sulphides into large test-tube or small beaker. Add 10 c.c. of $(\text{NH}_4)_2\text{CO}_3$ and heat for a few minutes. Filter.

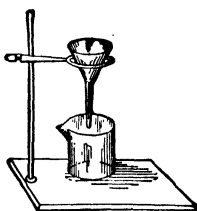


Sb, Sn, Au, Pt sulphides are on the paper.

Arsenic sulphide is in the filtrate.

Add HCl and Zn and make Gutzeit's test and if necessary Fleitmann's or Marsh's (page 33).

Dry this precipitate upon paper, and place paper and precipitate in a porcelain evaporator; add concentrated HCl and heat. (This *must* be done under the hood.) Dilute and filter, when Au and Pt will remain undissolved.



Au and Pt.

Sb and Sn.

To the Sb and Sn solution add a *little* Zn and a piece of platinum foil. The antimony and tin will both be reduced to the metallic state, the Sb being deposited on the Pt as a brown or black coating. The presence of Sb may be confirmed by removing the Pt, washing carefully, treating with $(\text{NH}_4)_2\text{S}$, and drying, when the coating will become Sb_2S_3 , orange-red.

To the solution to be tested for Sn add enough HCl to dissolve *all* the Zn which has been added; filter, and test filtrate with HgCl_2 (page 29).

Dissolve the insoluble residue of Au and Pt (the residue will be dark-colored if either of these metals are present) in aqua regia and divide solution into two parts.

Test one part for gold with solution of FeSO_4 , or a mixture of SnCl_2 and SnCl_4 (page 39).

Test the other part for Pt by adding NH_4Cl ; allow to stand

over night, adding a little alcohol, and a precipitate of ammonium platinic chloride, yellow and crystalline, will be obtained (see Plate I, Fig. 2).

OUTLINE SCHEME FOR ANALYSIS OF GROUP II.

To the warmed filtrate from Group I add H_2S . A ppt. may be sulphides of As, Sb, Sn, Au, Pt, Cu, Cd, Bi, Hg, and Pb.

Filter and treat with warm $(NH_4)_2S$.

Residue is Group II (a), page , and consists of sulphides of Cu, Cd, Bi, Hg, and Pb. Treat on paper c warm dil. HNO_3 .		Solution = As, Sb, Sn, Au, and Pt. Reprecipitate c HCl, filter and treat ppt. c strong $(NH_4)_2CO_3$ sol.	
Residue is Hg. Dissolve in aqua regia and test c $SnCl_2$ (page 29).	Solution Cu, Cd, Bi, and Pb. Add H_2SO_4 and filter.		Residue = Sb, Sn, Au, and Pt, sulphides. Treat c conc. HCl, dilute and filter.
	Ppt. is $PbSO_4$.	Solution is Cu, Cd, and Bi. Add NH_4OH and filter.	
	Ppt. is $Bi(OH)_3$.	Solution is Cu and Cd.	
	Test for Cu c H^+ and $K_4Fe(CN)_6$. (page 28.)	Test for Cd c KCN and H_2S .	
		Part I. Test for Au c $FeSO_4$ (page 39).	Part II. Test for Pt c NH_4Cl and alcohol.
		Solution. Sb and Sn. Test for Sb c Pt foil and Zn.	
		Solution. As. Make Gutzeit's or Fleitmann's test for As (page 33).	
		Test for Sn in filtrate c $HgCl_2$ (page 29).	

QUESTIONS ON GROUP II.

Why is it necessary to wash the precipitate of Group II practically free from Cl before dissolving in warm HNO_3 ?

How does the Hg found in Group II differ from the Hg in Group I?

Does the Pb found in Group II differ from the Pb in Group I?

Before making the final test for Sn, why is it necessary to dissolve *all* the Zn which has been added?

In precipitating Group II why should the solution be made acid with HCl before adding H_2S ?

Why is it better to use H_2S gas rather than H_2S water in precipitating metals of Group II?

Before testing for Cd, why add KCN to decolorize the copper solution?

Why is a confirmatory test for bismuth desirable?

Why must organic matter be destroyed before making Marsh's test for arsenic?

What reagent would you select for the precipitation of gold? Give reason for choice.

Why is sulphuric acid preferable to hydrochloric, in making Marsh's test for arsenic?

SALTS OF GROUP III METALS.

IRON

Compounds. — Iron forms two classes of salts, ferrous, represented by ferrous sulphate, FeSO_4 ; and ferric, represented by ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, or ferric chloride, FeCl_3 .

Ferric sulphate, also known as Monsel's salt, is used as a styptic.

Ferric chloride, FeCl_3 or Fe_2Cl_6 , is made by dissolving iron in hydrochloric acid, oxidizing the ferrous chloride with nitric acid, and then driving off the nitric acid by evaporation. The resulting solution, however, contains traces of free nitric and considerable free hydrochloric acid. In the tincture of chloride of iron, these acids react with the alcohol, forming various ethers, to which the peculiarities of the tincture may be due.

Copperas and green vitriol are commercial names for crystallized ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, which is used as a disinfectant and, to a slight extent, in medicine as an astringent.

Ferrous carbonate, $(\text{FeCO}_3)_x(\text{Fe}(\text{OH})_2)_y$, prepared by double decomposition between ferrous sulphate and potassium or sodium carbonate, is a medicinal preparation quite largely used, and known as "Blaud's pills."

Analytical Reactions. — A solution for demonstrating the reactions of ferrous salts is best made by saturating cold dilute sulphuric acid with clean iron wire. A 3 to 5 per cent solution of fresh crystals of ferrous ammonium sulphate may be used. The ordinary ferrous sulphate, or "copperas," is almost sure to contain some ferric salt. Use a 2 to 3 per cent solution of ferric chloride and make the following tests, comparing the deportment of the ferrous and ferric solutions with each reagent. Write the reactions.

H_2S with pure ferrous salts gives no reaction; with ferric salts the iron is reduced to the ferrous combination, but gives no precipitate except sulphur.

$(\text{NH}_4)_2\text{S}$ with ferrous iron gives a black precipitate of FeS ; with ferric salts it gives a precipitate containing FeS and S .

NH_4OH precipitates Fe^{II} as ferrous hydroxide, $\text{Fe}(\text{OH})_2$; the precipitate is white if perfectly pure, but is usually a dirty green from admixture of ferric compounds. The presence of NH_4Cl prevents a *complete* precipitation as $\text{Fe}(\text{OH})_2$.

With ferric salts, NH_4OH completely precipitates the iron as brick-red ferric hydroxide, $\text{Fe}(\text{OH})_3$.

$\text{K}_4\text{Fe}(\text{CN})_6$ with ferrous salts gives a bluish-white precipitate of potassium ferrous ferrocyanide, $\text{K}_2\text{FeFe}(\text{CN})_6$.

With a solution of ferric salts the deep Prussian blue, ferric ferrocyanide, $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$, is thrown out.

With potassium ferricyanide, ferrous salts give a dark-blue precipitate of ferrous ferricyanide, $\text{Fe}_3(\text{Fe}(\text{CN})_6)_2$. With ferric salts no precipitation occurs, but the color may change to green or brown.

KCNS or NH_4CNS gives no reaction with pure ferrous salts, but with ferric salts a deep red solution of ferric thiocyanate, $\text{Fe}(\text{CNS})_3$, is produced. This red color is destroyed by addition of HgCl_2 , not affected by HCl , and may be extracted from the aqueous solution by shaking with ether in which the $\text{Fe}(\text{CNS})_3$ is soluble.

ALUMINIUM

The most important soluble salts of aluminium are ammonia alum, $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, potash alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, and aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$.

Aluminium acetate is used technically in the waterproofing of fabrics.

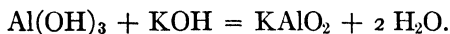
The term alum is applied to any salt of definite crystalline form containing one molecule of a univalent sulphate, such as K_2SO_4 or Na_2SO_4 , combined with one molecule of a trivalent sulphate, $\text{Al}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3$ or $\text{Cr}_2(\text{SO}_4)_3$, and crystallized with twenty-four molecules of water. The formula of alum, as given

above, comprises just one-half of this combination. Alum need not contain any aluminium whatever, as long as it conforms to the foregoing requirements; e.g., chrome alum may be $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ and ferric alum is usually $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$.

Analytical Reactions. — Use a 5 per cent solution of any soluble aluminum salt for the following tests:

$\text{Al}_2(\text{SO}_4)_3$ with $(\text{NH}_4)_2\text{S}$ and H_2O gives a white precipitate of $\text{Al}(\text{OH})_3$. Write the reaction.

$\text{Al}(\text{OH})_3$ is likewise produced by NH_4OH , Na_2CO_3 , or NaOH ; the precipitate is soluble in excess of fixed alkali hydroxides with formation of aluminates:



The alkaline peroxides produce aluminates from $\text{Al}(\text{OH})_3$. Demonstrate by covering a little precipitated aluminium hydroxide in a porcelain dish with a *very* little water; then sprinkle on to the mixture sodium peroxide in small portions till a clear solution results. Nitric or hydrochloric acid will decompose the aluminate, forming again the aluminium salt, which can be reprecipitated by ammonia as $\text{Al}(\text{OH})_3$.

The alkaline aluminates may also be formed by fusion with Na_2CO_3 and KNO_3 and then may be dissolved in hot water.

From the solution of KAlO_2 the Al may be precipitated as $\text{Al}(\text{OH})_3$ by excess of NH_4Cl (thus differing from Zn, page 52).

The presence of organic acids, tartaric, oxalic, etc., interferes with the precipitation of aluminium hydroxide and may entirely prevent it. The presence of ammonium chloride favors its precipitation.

CHROMIUM

Chromium forms two oxides; one, Cr_2O_3 , is basic in character, and forms the basis of chromic salts, as $\text{Cr}_2(\text{SO}_4)_3$, Cr_2Cl_6 (CrCl_3),* etc.; the other, CrO_3 , is an acid anhydride, crystallizes as dark-red needles, and gives rise to two series of salts: neutral chromates, such as K_2CrO_4 , and acid chromates or dichromates, $\text{K}_2\text{Cr}_2\text{O}_7$.

* There is a series of chromous salts, CrCl_2 , $\text{Cr}(\text{OH})_2$, etc., corresponding to a chromous oxide, CrO , but the oxide itself is not known.

Analytical Reactions. — The soluble chromic salts most easily obtained are chrome alum, $\text{KCr}(\text{SO}_4)_2$, chromic sulphate, $\text{Cr}_2(\text{SO}_4)_3$, and chromic chloride, CrCl_3 . With a 5 per cent solution of either of these the following may be demonstrated:

$\text{Cr}_2(\text{SO}_4)_3$ with $(\text{NH}_4)_2\text{S}$ gives greenish precipitate of $\text{Cr}(\text{OH})_3$.

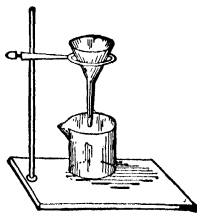
Similarly to aluminium, the chromium *hydroxide* is precipitated by the alkaline carbonates and the alkaline sulphides, as well as by the hydroxides; then, by boiling the $\text{Cr}(\text{OH})_3$ with NaOH or KOH , or by fusing with Na_2CO_3 and KNO_3 , or by the action of sodium peroxide and heat, chromates of the alkalies may be produced. The chromate, upon the addition of nitric acid, becomes the dichromate. This solution, after neutralization with ammonia, will give a characteristic yellow precipitate of PbCrO_4 with soluble salts of lead.

The solid dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, with strong H_2SO_4 gives, in the presence of chlorides, the reddish-brown gas CrO_2Cl_2 (chloro-chromic anhydride or chromium dioxychloride) used as a test for chlorides (page 79).

Analysis of Group III.

(Fe, Al, Cr. Phosphates and oxalates being absent.)

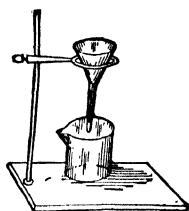
The filtrate from Group II must be freed from H_2S by boiling with a few drops of HNO_3 in a porcelain dish till a drop removed by a glass rod does not blacken filter-paper wet with a solution of lead acetate. This treatment also serves to oxidize the iron (reduced by H_2S) to ferric salt and at the same time concentrates the solution. To the clear solution thus obtained add 2 or 3 grams of solid NH_4Cl , then NH_4OH till alkaline, when the metals of this group will separate as hydroxides: $\text{Fe}(\text{OH})_3$ brick-red, $\text{Al}(\text{OH})_3$ white, $\text{Cr}(\text{OH})_3$ bluish-green. Filter and wash.



Group III.

Groups IV, V, and VI.

Transfer the precipitated hydroxides to a porcelain dish. Cover with a little water. Add, in small portions, sodium peroxide not exceeding in total bulk the original precipitate. Add a little more water and boil till oxygen ceases to be evolved, adding water if necessary to keep up the volume of the solution. Filter out iron if it is present.



$\text{Fe}(\text{OH})_3$.

Al and Cr as negative ions.

Wash the precipitate remaining on the paper (Fe) and dissolve in dilute HCl. Divide resulting solution (FeCl_3) into two parts and confirm presence of Fe by testing one with $\text{K}_4\text{Fe}(\text{CN})_6$ (blue precipitate) and the other with KCNS (red solution).

If iron is found, determine in original substance whether ferrous or ferric, by use of tests described on page 45.

To the filtrate containing sodium aluminate and chromate, add HNO_3 producing $\text{Al}(\text{NO}_3)_3$ and $\text{Cr}_2\text{O}_7^{=}$. Add 5 c.c. of 10 per cent NH_4Cl solution and make alkaline with NH_4OH , which precipitates $\text{Al}(\text{OH})_3$. Filter, acidify filtrate with acetic acid and test for presence of chromium with lead acetate solution. (Precipitate is PbCrO_4 .)

The presence of aluminium may be confirmed as follows:

Transfer the precipitate of aluminium hydroxide to a small evaporating dish, moisten with concentrated nitric acid, add a *very tiny* crystal of cobalt nitrate, and evaporate to dryness. Let the oxidizing flame of the Bunsen burner play directly upon the residue in the dish. Aluminium produces the blue cobalt aluminate.

The aluminium hydroxide should be as nearly white as possible. If it is dark in color, dissolve it in nitric acid and reprecipitate with ammonium hydroxide before treating with cobalt nitrate.

OUTLINE FOR ANALYSIS OF GROUP III.

Take clear filtrate from Group II and boil with a few drops of HNO_3 to expel H_2S and oxidize Fe'' . Add NH_4Cl and NH_4OH and filter.

Ppt. $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$. Treat with Na_2O_2 . Boil cH_2O . Filter (page 48).			Solution. Groups IV, V, and VI.
Ppt. $\text{Fe}(\text{OH})_3$. Test $\bar{\text{c}}$ KCNS and K_4Fe $(\text{CN})_6$ (page 45).	Sol. NaAlO_3 and Na_2CrO_4 . Add $\text{HNO}_3 = \text{Al}^{+++}$ and $\text{Cr}_2\text{O}_7^{=}$. Add $\text{NH}_4\text{OH} = \text{Al}(\text{OH})_3$ and $\text{CrO}_4^{=}$. Filter.		
Test for Al $\bar{\text{c}}$ $\text{Co}(\text{NO}_3)_2$ (page 48).	Test for $\text{CrO}_4^{=}$ $\bar{\text{c}}$ $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.		

QUESTIONS ON GROUP III.

Why boil off H_2S before precipitating the group with NH_4OH ?
Why add HNO_3 ?

In making final test for chromium, why is it necessary to acidify with acetic acid?

What is the action of the peroxide of sodium in the separation of aluminium and chromium?

Why is it necessary to test the original solution to determine the character of the iron?

SALTS OF GROUP IV METALS.

COBALT

Crystalline salts of cobalt are usually of pink color; anhydrous salts are blue.

Analytical Reactions. — $\text{Co}(\text{NO}_3)_2$ with $(\text{NH}_4)_2\text{S}$ gives precipitate of cobalt sulphide, black. Test solubility of this precipitate in HCl .

Make a borax bead by fusing a little borax on the looped end of a *clean* platinum wire. When a bead of clear "borax glass" has been obtained, dip it in a little of the cobalt sulphide just formed, and fuse again. The color of the bead when cold is a deep blue.

Note. — Be sure and make the fusion complete; the use of an insufficient amount of heat will account for much of the trouble experienced by students in obtaining satisfactory bead tests.

$\text{Co}(\text{NO}_3)_2$ with KNO_2 forms a double nitrite, $\text{Co}(\text{NO}_2)_2 \cdot 2 \text{KNO}_2$, soluble in water; but if sufficient acetic acid is added to produce a strong acid reaction, and the solution is heated, and then allowed to stand overnight, the cobalt is completely precipitated as another double salt, $\text{Co}(\text{NO}_2)_2 \cdot 3 \text{KNO}_2$, yellow and crystalline.

NICKEL.

Analytical Reactions. — Use a 2 per cent solution of the sulphate or nitrate. NiSO_4 with $(\text{NH}_4)_2\text{S}$ gives NiS , black. Test solubility in HCl .

The borax-bead test applied to NiS or other nickel salt gives a bead which is yellowish brown when cold, but the color is easily masked by other metals.

Ni salts with KNO_2 give the soluble double nitrate of similar composition to the Co salt, $\text{Ni}(\text{NO}_2)_2 \cdot 2 \text{KNO}_2$. The nickel salt, unlike the cobalt, is not easily decomposed, and is not precipitated by heating with acetic acid. Advantage is taken of this fact in effecting the separation of cobalt from nickel.

MANGANESE

The black oxide, manganese dioxide, is commercially important in the production of chlorine. By Weldon's process, the chlorine is obtained from hydrochloric acid, the MnO_2 acting as an oxidizing agent.

The oxidation of manganese dioxide in the presence of potassium hydroxide results in the formation of potassium permanganate, KMnO_4 . This salt is a valuable disinfectant and is largely used. Its decomposition furnishes five atoms of available oxygen from every double molecule ($\text{K}_2\text{Mn}_2\text{O}_8$.)

Condy's fluid, a commercial disinfectant, is a solution of potassium permanganate.

Manganese salts are usually flesh-colored.

Analytical Reactions. — A 3 per cent solution of the sulphate may be used in the following tests:

MnSO_4 with $(\text{NH}_4)_2\text{S}$ gives flesh-colored precipitate of MnS . Test solubility in HCl . With a little of the precipitated MnS , make a **RED-LEAD TEST** for Mn as follows:

Place in a test-tube a little red lead (Pb_3O_4). Add 3 or 4 cubic centimeters of a solution of nitric acid (about 1 part of concentrated HNO_3 and 1 of H_2O), and boil well. Add, by means of a glass rod, a little of the washed MnS to the mixture in the tube and boil again. Now dilute with water till the tube is about three-quarters full, and allow to stand till liquid is clear. If Mn is present, the supernatant fluid will show a pink or red color due to the formation of permanganic acid, HMnO_4 .

Note. — HCl or chlorides, even in small quantities, interfere with the reaction; hence it is recommended that the test be made on the sulphide. Reducing agents must likewise be absent. When these precautions are observed the test is a very simple and an extremely delicate one.

MnSO_4 with NaOH gives flesh-colored $\text{Mn}(\text{OH})_2$, insoluble in excess of reagent (separation from Zn).

Upon fusion with a mixture of KNO_3 and Na_2CO_3 , manganese salts produce green manganates, as Na_2MnO_4 .

ZINC

The oxide of zinc combines with phosphoric acid and is peculiarly adapted to the preparation of dental cements. Zinc salts with alkaline carbonates precipitate a white basic carbonate, $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$, which is used as a pigment in the preparation of paint and also as a source of pure oxide of zinc.

The sulphate, ZnSO_4 , also known as white vitriol, is perhaps the most common salt. The chloride is a constituent of many commercial liquid disinfectants and antiseptics. The nitrate also is easily obtained.

A 2 or 3 per cent solution of any of these soluble salts may be used in the following tests:

Analytical Reactions. — ZnSO_4 with $(\text{NH}_4)_2\text{S}$ gives a white precipitate of ZnS .

Sulphide of zinc is the only white *sulphide* formed in the course of analysis of ordinary solutions, but the following white precipitates are formed: Sulphide of manganese is flesh-colored or dirty white. Aluminium hydroxide resembles sulphide of zinc in appearance and is precipitated by $(\text{NH}_4)_2\text{S}$. Yellow $(\text{NH}_4)_2\text{S}$ added to an acid solution will precipitate sulphur, white, very fine and difficult to filter out.

ZnSO_4 with NaOH (or KOH) gives a white gelatinous precipitate of zinc hydrate, $\text{Zn}(\text{OH})_2$, soluble in excess of the reagent as Na_2ZnO_2 (sodium zincate).

Note. — Colorless gelatinous precipitates in slight amounts may escape detection, as it sometimes takes careful observation to see them, especially if the laboratory light happens to be poor.

Na_2ZnO_2 with H_2S or $(\text{NH}_4)_2\text{S}$ gives precipitate of ZnS .

From solution of Na_2ZnO_2 the Zn may be precipitated as $\text{Zn}(\text{OH})_2$ by addition of NH_4Cl , but further addition of the NH_4Cl redissolves the precipitate (distinction from Al , page 46).

ZnSO_4 with $\text{K}_4\text{Fe}(\text{CN})_6$ gives white precipitate of zinc ferrocyanide ($\text{Zn}_2\text{Fe}(\text{CN})_6$), insoluble in NH_4OH .

Note. — The ferrocyanide and the sulphide are the only two zinc salts not soluble in NH_4OH . (Prescott and Johnson, page 179.)

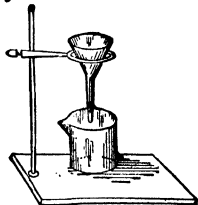
Soluble zinc salts, with oxalic acid or oxalates, give a precipitate of zinc oxalate sufficiently insoluble in alcohol and water to make it available for use in the quantitative separation of zinc from dental alloys. The crystals have a characteristic form, which may be recognized under a microscope (Plate I, Fig. 6, p 65).

Analysis of Group IV.

(Co, Ni, Mn, Zn.)

(In the presence of phosphates, oxalates, borates, etc., examine this group by the scheme given on page 71.)

To the clear filtrate from Group III add $(\text{NH}_4)_2\text{S}$. A precipitate may be NiS ,* CoS , MnS , and ZnS . Wash the precipitate and treat with *cold dilute* HCl , which will dissolve MnS and ZnS only.



CoS and NiS , black.

MnCl_2 and ZnCl_2 in solution.

Make a borax-bead test (page 49) of the precipitates on funnel

* A black precipitate persistently passing through the paper is NiS , and sometimes requires heating or concentrating before a clear filtrate can be obtained.

in above figure. If a clear red-brown bead is obtained, Ni alone is present. If the bead is blue, Co is present, Ni may or may not be.

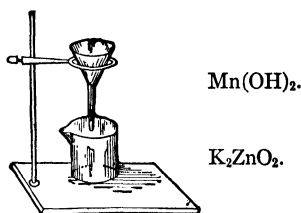
Separation of Cobalt and Nickel.

If Co is present, dissolve the black precipitate off the paper with aqua regia, evaporate in porcelain capsule practically to dryness, dissolve in H_2O , add excess of acetic acid and potassium nitrite (KNO_2). Allow to stand over night, when Co will separate out as a yellow crystalline precipitate (page 50).

Filter and test filtrate for Ni with NaOH, which gives a pale-green precipitate of $Ni(OH)_2$ insoluble in excess of the precipitant.

Separation of Manganese and Zinc.

Boil the HCl solution of Zn and Mn to expel the H_2S , then add a decided excess of KOH or NaOH and allow to stand ten minutes *without* heating. Mn will separate out as $Mn(OH)_2$, while Zn will remain in solution as K_2ZnO_2 .



Test precipitate by the red-lead test for Mn, page 50. Test filtrate for Zn by adding H_2S or a few drops of $(NH_4)_2S$, which will precipitate ZnS , white.

OUTLINE FOR ANALYSIS OF GROUP IV.

To filtrate from Group III add $(NH_4)_2 S$. Filter.

Ppt. = CoS, NiS, ZnS, MnS. Treat $\bar{c}$ dil. HCl.			
Residue. Co and Ni. Make borax bead test. Separate Co by means of KNO_2 (page 50)	Sol. Mn and Zn. Boil and heat $\bar{c}$ KOH or NaOH.		
	Ppt. $Mn(OH)_2$. red-lead test	Make	Sol. K_2ZnO_2 . Add H_2S = ppt. ZnS (page 52)

QUESTIONS ON GROUP IV.

Why dissolve the MnS and ZnS in *cold* and *dilute* HCl ?

Why is it necessary to separate *all* the Mn before testing for Zn ?

If traces of Co or Ni are dissolved by the HCl , how does it affect the final test for Zn ?

In this analysis (in absence of phosphates, etc.) what important difference between the behavior of salts of Zn and Al ?

Why is it necessary to allow time for *complete* precipitation of Co with KNO_2 ?

Why expel H_2S before separating Mn ?

Where does this H_2S come from?

SALTS OF GROUP V METALS.

THE ALKALINE EARTHS Ba , Sr , Ca , Mg .

The common alkaline earth metals present similarity of properties which ally them more closely than the metals of some of the previous analytical groups. None of the metals occur free in nature. The metals themselves are isolated with considerable difficulty, with the exception of magnesium, and they all decompose water with evolution of hydrogen, calcium, strontium, and barium producing the decomposition at ordinary temperatures, magnesium, at high temperatures only.

As a group they form insoluble carbonates, from which carbon dioxide is easily driven off by heat, leaving the oxide of the metal. This oxide unites with water, forming feebly soluble hydroxides. The solutions of the hydroxides are alkaline to litmus, and are used, to a considerable extent, in medicine, as antacids.

There are two other metals belonging to this group. The first, glucinum, also called beryllium, has an atomic weight of 9.1. Soluble salts of glucinum are precipitated by ammonium hydroxide as white and gelatinous beryllium hydroxide. The precipitate somewhat resembles aluminium hydroxide. Ammonium carbonate also precipitates the hydroxide, which is easily soluble in excess of reagent. The solution, however, should

not be boiled, as prolonged boiling will cause the beryllium hydroxide to reprecipitate.

Beryllium oxide unites with phosphoric acid, forming a phosphate similar in its properties to the basic phosphate of zinc, and its use is claimed by some manufacturers to be essential to the preparation of artificial enamels. (See page 137.)

The second rare metal belonging to this group is radium; atomic weight 226.4. The metal itself has not as yet been isolated. Its compounds are obtained from uraninite or pitchblende, a source of uranium. It is bivalent, and the chlorides, bromides, nitrates, and hydroxides have been studied.

Radium compounds are luminous, and the active emanations emitted by them have been condensed at 150° below zero Centigrade, forming new substances, among which helium has been identified. The discovery of this fact is responsible for our new conception of the divisibility or disintegration of what were once considered indivisible atoms, also of the "smoke ring" molecule, and the possible transmutation of the elements.

BARIUM

Barium, the next metal to radium in this group, in point of atomic weight, which is 137.37, occurs chiefly as a sulphate BaSO_4 , heavy spar, and BaCO_3 , witherite. Barium oxide may be formed by heating the carbonate or nitrate to red heat. It absorbs oxygen from the air with formation of the binoxide BaO_2 . This in turn is decomposed, oxygen being given off and BaO being reproduced. The barium oxide hence becomes a source of oxygen of commercial importance. The cost of producing oxygen by this method is obviously small.

The peroxide of barium is also of particular importance to the dentist, in that it is an important source of peroxide of hydrogen. This substance is considered more fully in a chapter on mouth washes and local anesthetics in Vol. II.

Barium hydroxide, Ba(OH)_2 , slightly soluble in water, absorbs CO_2 very rapidly and may be used as a test for this gas. The solution is known as "Baryta Water."

Analytical Reactions. — Use a two per cent solution of the chloride for tests.

BaCl_2 with $(\text{NH}_4)_2\text{CO}_3$ gives white precipitate of barium carbonate. Test solubility in acids. With soluble sulphates BaCl_2 produces BaSO_4 insoluble in HCl . (Test for sulphates.)

BaCl_2 with $\text{K}_2\text{Cr}_2\text{O}_7$ or K_2CrO_4 gives yellow precipitate of BaCrO_4 . Barium salts moistened with HCl and held on a clean platinum wire give to the colorless flame of the Bunsen burner a green or yellowish-green color.

STRONTIUM

Atomic weight 87.63. Occurs as the carbonate, SrCO_3 , strontianite, also as the sulphate.

Strontium salts are used commercially in the preparation of colored fires, strontium imparting a vivid red color to the flame. Strontium oxalate crystallizes in practically the same forms and much more easily than calcium oxalate.

Analytical Reactions. — Use a 3 to 4 per cent solution of the nitrate or chloride for tests.

$\text{Sr}(\text{NO}_3)_2$ with $(\text{NH}_4)_2\text{CO}_3$ gives white precipitate of SrCO_3 .

$\text{Sr}(\text{NO}_3)_2$ with H_2SO_4 or soluble sulphate gives white precipitate of SrSO_4 , rather more soluble in water and more slowly formed than BaSO_4 .

A saturated solution of SrSO_4 may be used to test for barium in presence of Sr salts.

$\text{Sr}(\text{NO}_3)_2$ with K_2CrO_4 gives precipitate of SrCrO_4 , but with the acid chromate (dichromate) of potassium, $\text{K}_2\text{Cr}_2\text{O}_7$, no precipitate is formed except in concentrated solutions.

$\text{Sr}(\text{NO}_3)_2$ with oxalic acid gives a precipitate of strontium oxalate, SrC_2O_4 , crystallizing in the so-called envelop form (Plate I, Fig. 3, page 65). Salts of Sr color the Bunsen flame crimson.

CALCIUM

Atomic weight 40.07. Calcium is widely distributed and very abundant, limestone, chalk, marble, and calc-spar being natural carbonates CaCO_3 ; gypsum and alabaster are sulphates.

Calcium phosphate occurs in the mineral apatite and is also a principal constituent of animal bones.

Plaster of Paris. — Calcium sulphate is of particular interest, occurring as gypsum, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$. Upon heating, the two molecules of water of crystallization may be driven off, leaving the anhydrous CaSO_4 , or plaster of Paris, so largely used in dental laboratories. If the heat used is too high, a "dead burnt" plaster results which unites so slowly with water as to be practically useless. More careful dehydration at a lower temperature yields a so-called "soluble anhydrite" which absorbs water rapidly. The best plaster for dental purposes is neither of these, but a product which contains one molecule of water to every two of calcium sulphate. This is known as the half hydrate and is the chief constituent of plaster of Paris. This half hydrate has a property of setting with more or less of a fibrous character which permits its use in the formation of plaster casts. Essig states that if, in the preparation of plaster, the heat is allowed to exceed 127°C ., its affinity for water is impaired or destroyed and this effect will not be produced.*

As plaster sets, more or less expansion takes place, and the mass, if spread upon glass, usually rises slightly in the center, producing a plate which is somewhat concave on the under surface. This tendency to expansion varies with different grades of plaster, as may easily be shown by a method suggested by Dr. George H. Wilson in the *Dental Cosmos* for August, 1905, page 940; this method consists simply of filling small glass beakers with mixtures similarly prepared. Some samples were found to expand so slightly as not to injure the glass, others cracked, and some broke the beaker into fragments.

In the *Dental Cosmos* for 1908, page 67, Dr. J. H. Prothero of Chicago shows that plaster, during the first four minutes,

* American Text-book of Prosthetic Dentistry.

gives a slight contraction, and is then stationary for about forty-five seconds. Then it expands with increasing rapidity, the maximum movement attained being one-thousandth of an inch per minute for about ten minutes. After half an hour the movement practically ceases. The slightest possible trace of potassium sulphate added to the water used in mixing and the least possible agitation reduces both the rate and the amount of expansion.

The method of mixing also affects the amount of expansion. In a valuable article on "Experiments in Plaster of Paris to Test Expansions," by Dr. Stewart J. Spence, in *Items of Interest*, 1902, page 721, it is shown that "not only do different plasters expand in differing degrees, but the same plaster expands very differently according to the stirring given it before pouring," and that long stirring increases the heat developed, the rapidity of setting, and the amount of expansion, but decreases the strength.

Various methods have been prepared to overcome the difficulties in manipulation of plaster, such as mixing the plaster with alum, marble-dust, or potassium sulphate. A compound on the market consists of a mixture of plaster and Portland cement. A mixture which has been very strongly recommended as an investment preparation consists of two-thirds plaster and one-third powdered pumice-stone.

Analytical Reactions. — Use a 3 or 4 per cent solution of CaCl_2 for tests.

CaCl_2 with $(\text{NH}_4)_2\text{CO}_3$ gives white precipitate of CaCO_3 , easily soluble in acids.

CaCl_2 with oxalic acid or soluble oxalates gives a white precipitate of CaC_2O_4 , similar in form to the SrC_2O_4 but much more difficult to obtain in the crystalline condition.

CaSO_4 is not precipitated except from moderately concentrated solution.

A saturated solution of CaSO_4 may be used to test for strontium salts in presence of Ca.

MAGNESIUM

Epsom salt, or magnesium sulphate, occurs as a constituent of laxative waters. The crystallized salt, $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$, resembles oxalic acid in appearance, and has been mistaken in several instances for the poisonous acid.

Magnesium carbonate is used in pharmacy in two forms; viz., the light and the heavy. These are produced by precipitating dilute or concentrated solutions of magnesium sulphate with sodium carbonate.

The light and heavy magnesium oxides are produced by calcination of the light or heavy carbonates. Magnesium salts are quite generally distributed in the human system, but in small quantities. They occur in the bones, the teeth, and the various body fluids.

Analytical Reactions. — A 5 per cent solution of the sulphate or nitrate may be used in the following tests:

Magnesium salts with $(\text{NH}_4)_2\text{CO}_3$ give a white precipitate of basic carbonate of variable composition. This precipitate forms *very* slowly in dilute solution, and in the presence of NH_4Cl the formation of soluble double salts prevents the precipitation altogether.

MgCl_2 with Na_2HPO_4 gives in fairly concentrated solution a white precipitate of MgHPO_4 . In presence of NH_4Cl and NH_4OH the alkaline phosphates precipitate magnesium-ammonium-phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$, even from *very* dilute solution (Plate I, Fig. 5).

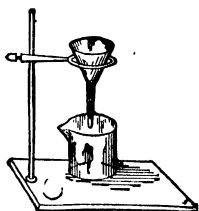
In case the precipitate has formed very slowly, it may separate as small, almost transparent, crystals clinging to the sides of the beaker.

Ammonium oxalate does not precipitate magnesium solutions.

Analysis of Group V.

(Ba, Sr, Ca, Mg.)

To the filtrate from Group IV containing NH_4Cl and NH_4OH , add $(\text{NH}_4)_2\text{CO}_3$. (If NH_4Cl and NH_4OH are not present, add 10 c.c. of NH_4Cl solution and NH_4OH till strongly alkaline, before proceeding with the analysis.) Ba, Sr, and Ca will be precipitated as carbonates; Mg will be held in solution by the ammonium chloride. Filter.



Ca, Ba, Sr carbonates.

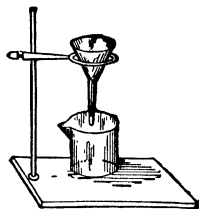
Mg and metals of Group VI.

Test the filtrate for Mg by adding Na_2HPO_4 , when a white crystalline precipitate is $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$.

To the carbonates on the paper add dilute acetic acid, which will dissolve the precipitate, forming acetates of the three metals.

Take a *portion* of the acetate solution in a test-tube and make a preliminary test for Ba by adding *acid* chromate of potassium ($\text{K}_2\text{Cr}_2\text{O}_7$). A yellowish precipitate will be BaCrO_4 .

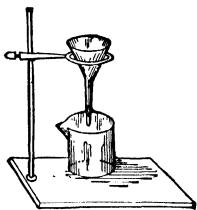
If *Ba is present*, add $\text{K}_2\text{Cr}_2\text{O}_7$ to the whole of the solution and filter out the BaCrO_4 .

 BaCrO_4 .Sr and Ca acetates, $\text{K}_2\text{Cr}_2\text{O}_7$, etc.

It is desirable to remove the excess of bichromate from the filtrate before testing for Ca and Sr.* To do this add NH_4OH

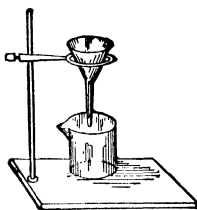
* The object of removing the $\text{K}_2\text{Cr}_2\text{O}_7$ is to furnish a colorless solution wherein the Sr or Ca precipitates may be more clearly discerned. It is not absolutely necessary and, in case the amount of Sr and Ca is probably slight, might be omitted, as the operation is always attended with some loss.

till alkaline; then $(\text{NH}_4)_2\text{CO}_3$ will precipitate SrCO_3 and CaCO_3 . Filter and dissolve off the paper with acetic acid as before.



CaCO_3 and SrCO_3 , which when treated with acetic acid, will give a solution of the acetates of Ca and Sr.

Reserve about one-fourth of this acetate solution. To the remainder add dilute K_2SO_4 solution, which will precipitate SrSO_4 . (If only slight amounts of Sr are present, it may take some time to complete the precipitation. If a large amount of Ca is present, some CaSO_4 may also be thrown down.) Filter.



SrSO_4 .

$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ or CaSO_4 .

Test filtrate for Ca by adding ammonium oxalate, which will precipitate calcium oxalate, white.

If there is any question about the precipitate thrown out by K_2SO_4 being Sr, make confirmatory test on reserved portion, either by flame test (page 56), or by adding CaSO_4 , and allowing to stand twelve hours. CaSO_4 will precipitate Sr as SrSO_4 , but of course cannot reprecipitate Ca.

QUESTIONS ON GROUP V.

Why add NH_4Cl before precipitating the group with $(\text{NH}_4)_2\text{CO}_3$?

Why dissolve the precipitated carbonates in acetic acid rather than HCl ?

Why use the acid chromate of potassium ($\text{K}_2\text{Cr}_2\text{O}_7$) in testing for Ba rather than the neutral chromate (K_2CrO_4)?

Why precipitate Sr and Ca after separation of Ba with $\text{K}_2\text{Cr}_2\text{O}_7$?

OUTLINE SCHEME FOR ANALYSIS OF GROUP V.

To clear filtrate from Group IV add $(\text{NH}_4)_2\text{CO}_3$.*Precipitate* = Ba, Sr, and Ca. Add $\text{K}_2\text{Cr}_2\text{O}_7$, if necessary to precipitate Ba.*Solution* = Mg. Test for Mg with Na_2HPO_4 (page 59).*Precipitate* = BaCrO_4 .*Solution* = Sr and Ca. Reprecipitate Sr or Ca with $(\text{NH}_4)_2\text{CO}_3$. Dissolve in $\text{H}\bar{\text{A}}$. Remove Sr with K_2SO_4 and alcohol, and test filtrate for Ca with $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

SALTS OF GROUP VI METALS.

THE ALKALINE METALS, K, Na, NH_4 , Li.

Potassium, sodium, and the hypothetical "metal" ammonium are the bases of a very large number of salts used in the arts and sciences.

As a class these metals may be distinguished from the alkaline earths by the ready solubility of their hydrates and carbonates. The hydrates of the alkaline earths are only sparingly soluble, and their carbonates are insoluble.

The salts of lithium are also soluble, but are used in relatively small amounts.

These bases are not precipitated by any group reagent and must be detected by individual tests.

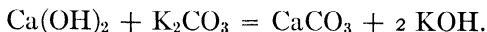
POTASSIUM.

Atomic weight 39.1. Occurs as carbonate in wood ashes, as nitrate in the "niter beds" of India, etc., as chloride from the Stassfurt deposit in the Province of Saxony, Prussia, as the mineral sylvite, also in the double chloride of magnesium and potassium (carnallite).

Properties. — Melting-point 62.5° . Potassium is a silver white metal. It decomposes water at ordinary temperatures, evolving enough heat to ignite the liberated hydrogen.

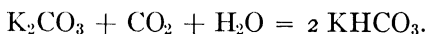
Compounds. — The salts of potassium are generally soluble in water. Among the more important compounds is the hydroxide KOH. This is used very largely as a starting point in the preparation of many of the medicinal salts of potassium. It

may be made by treating potassium carbonate with slaked lime, according to the following reaction:



The carbonate obtained from wood ashes is known as "salts of tartar," and in the impure form as pearl ash. Potassium carbonate is also made in large quantities from the native chloride found in the Stassfurt deposit.

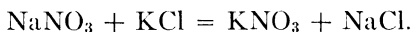
The bicarbonate KHCO_3 , or saleratus, may be obtained by saturating the carbonate with CO_2 .



This salt, used in cooking, proves more or less irritating, and has been practically replaced by the corresponding sodium salt, NaHCO_3 or "cooking soda."

Potassium nitrate, KNO_3 , also called niter and saltpeter, is used in medicine as a diuretic. As it gives off oxygen easily, and is consequently a good oxidizing agent, it is a constituent of fireworks, gunpowder, etc.

KNO_3 may be prepared from the cheaper sodium nitrate by double decomposition with potassium chloride.



Potassium bromide, used as a sedative, may be prepared by treating caustic potash, KOH , with bromine.



The bromate, KBrO_3 , is separated by crystallization.

Potassium iodide may be made in a similar manner by substituting iodine for the bromine. Potassium iodide is very soluble, being dissolved in less than its own weight of water. In the laboratory, potassium iodide is used as a solvent for iodine, and as a reagent.

Potassium cyanide, KCN , an extremely poisonous compound, is used by jewelers for cleaning silver, etc., and in the arts for the preparation of double salts used in electro-plating. It is decomposed by CO_2 , forming K_2CO_3 and liberating hydrocyanic acid.

Potassium ferrocyanide and ferricyanide are considered under cyanogen compounds in Vol. II, Chapter 5.

Potassium chlorate may be prepared by treating a hot solution of the hydroxide with chlorine gas. The reaction is the same as that given for the preparation of the bromide, and results in five molecules of the potassium chloride to one of the chlorate.

Potassium sulphide, K_2S , is soluble in water, and, in common with other alkaline sulphides, is a solvent for sulphur, thereby forming a number of polysulphides.

The pentasulphide, K_2S_5 , is known as "liver of sulphur" or sulphuret of potassium.

Potassium platonic chloride, K_2PtCl_6 , and potassium acid tartrate, $KHC_4H_4O_6$, are only sparingly soluble and may be precipitated by addition to the solution of an equal volume of alcohol, in which they are quite insoluble.

The potassium acid tartrate, or bitartrate, is also called cream of tartar, and is used in the manufacture of baking powder. This salt separates from wine vats, being precipitated by the alcohol produced during the process of fermentation of the grape juice. In this impure form it is known as argols, or crude tartar.

Analytical Reactions. — The presence of potassium salts may be detected spectroscopically or by the violet color given to the flame observed through blue glass. Make comparative tests with known solutions of sodium and potassium salts, using blue glass of sufficient thickness to obscure the yellow (Na) ray.

Note. — In making the flame test the best results are obtained by evaporating a little of the *original* solution to dryness, moistening with HCl and then taking up on a loop of clean platinum wire.

The platonic chloride test may be made as follows:

Add a few drops of HCl to a little of the solution, then evaporate to dryness. Keep at a low red heat till all ammonium salts have been driven off, cool, and take up in a little (not more than 5 c.c.) distilled water. Add a few drops of H_2PtCl_6 and about 5 c.c. of alcohol. Set aside for some time. Yellow K_2PtCl_6 will crystallize out and will be recognizable under the microscope (Plate I, Fig. 4).

PLATE I.—QUALITATIVE ANALYSIS.

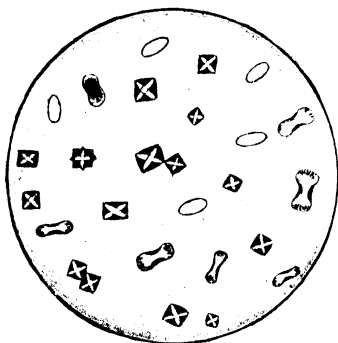


FIG. 1.
Calcium Oxalate.

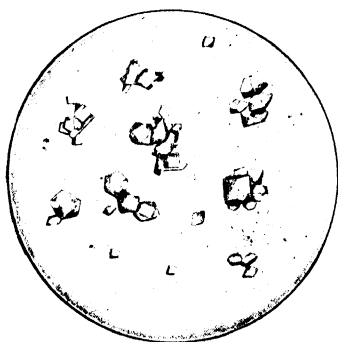


FIG. 2.
Ammonium Platinic Chlorid.

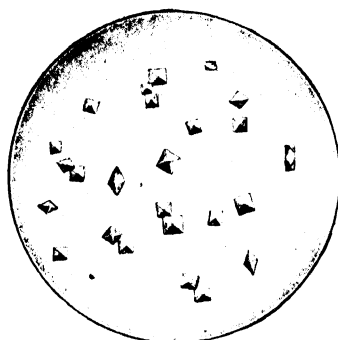


FIG. 3
Strontium Oxalate.

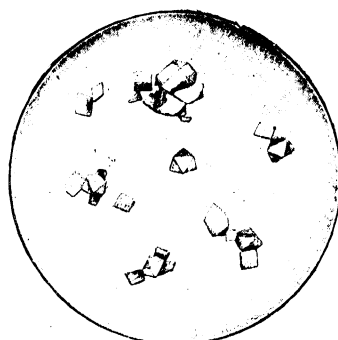


FIG. 4.
Potassium Platinic Chlorid.



Magnesium Ammonium Phosphate.

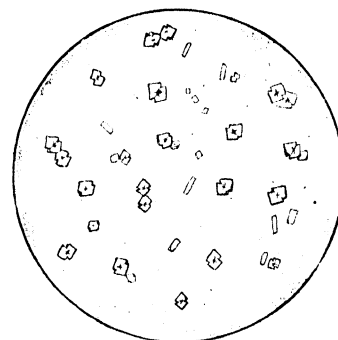


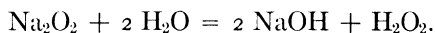
FIG. 6.
Zinc Oxalate.

SODIUM

Atomic weight 23.0. It occurs principally as chloride in sea-water and in mineral deposits, and to a lesser extent as nitrate, Chili saltpeter, and as cryolite, the double fluoride of aluminium and sodium, (Na_3AlF_6), found in Greenland.

Properties. — Melting-point 95.6° . Sodium is a shiny metal of cheese-like consistency, easily cut with a knife. It tarnishes quickly in the air, with the formation of the hydroxide. Sodium, as well as potassium, can be distilled in atmospheres which do not affect the metal.

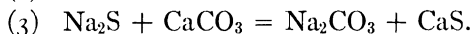
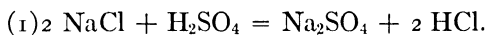
Compounds. — Sodium peroxide, or dioxide, Na_2O_2 , may be prepared by simply heating metallic sodium in dry air. It is a yellowish-white powder used to some extent in dental practice for the preparation of alkaline solutions of H_2O_2 :



The alkaline peroxide is much more efficient as a bleaching agent than the neutral or acid preparations.

Sodium hydroxide, NaOH , is found in trade in several forms. The stick "caustic soda," used in chemical laboratories, contains from 5 to 30 per cent of water. In a powder form, less pure than the above, it is known as "concentrated lye," Babbitt's potash, etc., and is used for cleaning, and in the manufacture of soap. Sodium hydroxide is caustic or escharotic in its action upon animal tissue.

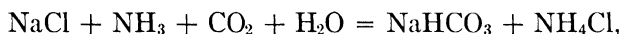
Sodium carbonate, Na_2CO_3 , crystallizes with ten molecules of water. In this form it is known as "sal soda," or washing soda. It is used as a starting point in the manufacture of other sodium salts. Sodium carbonate is produced from sodium chloride by the Le Blanc process, in which the following reactions are involved:



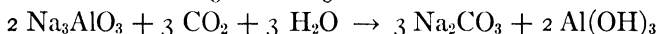
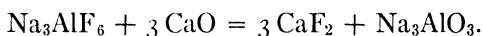
The last two reactions are combined in the actual process of manufacture, and the mixture of sodium sulphate, carbon, and

calcium carbonate is heated; from the resulting "black ash," pure sodium carbonate is produced.

More recent processes are the Solvay or ammonia process, depending on the following reaction:



and the cryolite process, in which the source of the sodium is the double fluoride of sodium and aluminum, Na_3AlF_6 . By this process the cryolite is heated with lime, forming calcium fluoride and sodium aluminate.



Note. — According to Remsen the sodium aluminate probably consists of a variety similar in composition to the potassium aluminate given on page 46 (NaAlO_2 and Na_2O until water is added).

Sodium bicarbonate, NaHCO_3 , also called cooking soda, is largely used like "saleratus" (KHCO_3) as a source of carbon dioxide in the leavening or aerating of bread.

Sodium bicarbonate is hydrolized by water, i.e., it dissociates in solution, forming sodium hydroxide and carbonic acid. The carbonic acid is a weak acid furnishing very few hydrogen ions, while the hydroxide is a strong base. It follows that the reaction of such a solution is alkaline to litmus, although the salt answers to our definition of an acid salt. This is true of sodium carbonate (the products of hydrolysis being NaOH and NaHCO_3), and in a similar manner of corresponding potassium salts.

Sodium chloride, NaCl , common salt, exists in sea-water to the extent of 2.7 per cent, and some of it is obtained from this source, although the greater amount is produced by the salt mines. Salt is a constituent of all of the body fluids, and can be easily obtained as cubical crystals by the evaporation of urine or of dialyzed saliva.

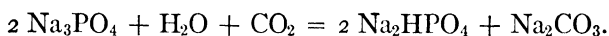
Physiological, or normal, salt solution contains about 0.7 per cent of sodium chloride, and has practically the same osmotic pressure as blood.

The term "physiological" is to be preferred to the term "normal," as the latter is also properly applied to a solution

used in volumetric analysis containing exactly 5.85 per cent of sodium chloride (see page 155).

Sodium nitrate, NaNO_3 , Chili saltpeter, is valuable as a fertilizer, but too hygroscopic to be used in the same way as potassium nitrate, in the preparation of gunpowder, fireworks, etc.

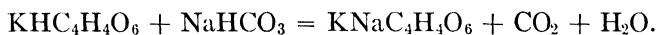
Sodium phosphate, trisodic phosphate, Na_3PO_4 , is a crystalline salt, soluble in water, but of slight interest in Dental Chemistry. It is easily decomposed by CO_2 , forming Na_2HPO_4 and Na_2CO_3 .



The disodic phosphate, Na_2HPO_4 , also called neutral or orthosodium phosphate, is the sodium phosphate of the Pharmacopœia. It is faintly alkaline in reaction, and exists in the body fluids generally. The alkaline reaction (to litmus) of saliva is, in part, due to its presence.

The acid, or monobasic sodium phosphate, NaH_2PO_4 , is a translucent crystalline salt found to some extent in the body fluids, particularly the urine, to the acidity of which it is probably a contributing factor, although to a much less extent than was formerly supposed.

Sodium potassium tartrate, $\text{KNaC}_4\text{H}_4\text{O}_6$, Rochelle salt, is used in medicine as a mild laxative. It is the product of the double decomposition incident to raising bread with "cream of tartar and soda."



Sodium sulphate crystallized with ten molecules of water ($\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$) is known as Glauber's salt.

Analytical Reactions. — Sodium may be detected by the use of the spectroscope or by the *persistence* of the yellow flame obtained with a *clean* platinum wire and a colorless Bunsen flame. Make a comparative test with a small amount of known sodium salt.

Sodium salts, with only a very few exceptions, are soluble. The pyroantimonate, $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$, may be precipitated in the

cold by a freshly prepared solution of *potassium* pyroantimonate. (Prescott and Johnson's "Qualitative Chemical Analysis," page 228.)

From a solution stronger than 3 per cent and nearly neutral, the double acetate of uranyl and sodium ($\text{NaC}_2\text{H}_3\text{O}_2, \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$) may be precipitated. (Fig. 5.)

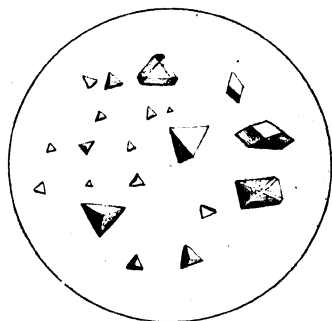


FIG. 5. — Uranyl Sodium Acetate.

As triple crystalline acetates may also be formed with Mg, Cu, Fe, Ni, and Co, it is advisable to first precipitate the bases of the first five groups and drive off ammonium salts, as in the test for K with H_2PtCl_6 .*

LITHIUM.

Atomic weight 6.94. The carbonate, citrate, bromide, and chloride are used in medicine.

The value of lithium salts as uric acid solvents is questionable, because of the insolubility of the phosphate.

The presence of lithium is easily shown after the precipitation of strontium by the intense carmine color given to the Bunsen flame.

The spectroscope furnishes a very delicate and positive test for this element.

AMMONIUM.

Ammonia is obtained in large part from the ammoniacal liquor of the gas works, where illuminating gas is made by the distillation of coal. The liquor, charged with ammonia, is treated with hydrochloric or sulphuric acid, thus producing an impure salt which is subsequently purified or used as a source of NH_3 in the preparation of pure ammonium compounds.



Compounds. — Ammonium hydroxide, NH_4OH , has never been separated as such, free from water. It undoubtedly exists, however, in aqueous solutions of ammonia gas.

* Behren, Manual of Microchemical Analysis, page 32.



The negative hydroxyl ions of this ammonium base are not separated by dissociation to the same degree as those of potassium hydroxide in solution; hence, it is a weaker base.

Aqua ammonia of the Pharmacopeia contains 10 per cent NH_3 . The "stronger water of ammonia," containing 28 per cent of the gas, is about as strong a solution as it is safe to make for shipment, and containers should never be more than four-fifths full. The 28 per cent solution is referred to as 26° ammonia, the degrees indicating the specific gravity as taken by the Baumé hydrometer.

Ammonium carbonate exists in solution. The salt used in medicine under this name is really a mixture of ammonium bicarbonate, NH_4HCO_3 , and the carbamate, $\text{NH}_4\text{NH}_2\text{CO}_2$.

This salt gives off NH_3 gas, and, moistened with ammonia water and perfumed, constitutes "smelling salts."

Ammonium chloride, sal ammoniac (NH_4Cl), white, crystalline, is made by neutralizing NH_4OH with hydrochloric acid. Ammonium chloride will sublime unchanged. It is freely soluble in water; its solution acts as an electrolyte and will dissolve metals from an alloy. If a silver-plated spoon is allowed to remain for ten or twelve hours in a dilute solution of ammonium chloride, an appreciable amount of copper will pass into solution, coloring it blue or green, according to the concentration of the copper solution. It also dissolves some metallic oxides, as zinc oxide.

As saliva is known to contain considerable NH_4Cl , the above facts should be studied carefully in considering the action of saliva on substances used for filling teeth, although the solvent action of NH_4Cl in saliva is not nearly as great as it is in water.

Ammonium nitrate, NH_4NO_3 , crystallizes in large six-sided prisms without water of crystallization. It is very soluble in water. It melts at 165° C. Heated at 210° C., it decomposes into nitrous oxide and water. Above 250° C., other oxides of nitrogen are produced; therefore, in the preparation of nitrous

oxide for dental anesthesia, care should be taken to keep the temperature of the reaction between these limits.

Ammonium acetate, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. A solution of this salt, containing about 7 per cent, is used in medicine as a diaphoretic. The solution is also known as Spirit of Mindererus. In analytical chemistry, it is used as a solvent for lead sulphate.

Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, is a white crystalline salt soluble in water, not used medicinally, but largely used as a reagent in physiological chemistry. It melts at 140°C. , and at a higher temperature it decomposes.

Ammonium sulphide, $(\text{NH}_4)_2\text{S}$, is used as a solvent and reagent. It may be prepared by saturating ammonia water, NH_4OH , with H_2S , then adding an equal volume of ammonia water:



A polysulphide, made by dissolving sulphur in $(\text{NH}_4)_2\text{S}$ is the reagent used in dissolving the sulphides of Group II (b) and in precipitating the zinc group.

Ammonium phosphates. Ammonium, like other univalent bases, is capable of forming, with phosphoric acid, three different salts. $(\text{NH}_4)_3\text{PO}_4$ is very unstable. The diammonium phosphate has been used, to a slight extent, in medicine (Br. P.) and has been shown to be an energetic activator of lactic acid organisms.*

The importance of this fact, in relation to dental caries, has yet to be demonstrated.

Microcosmic salt is a name given to a double ammonium sodium phosphate $(\text{NH}_4\text{NaHPO}_4 \cdot 4\text{H}_2\text{O})$ used in blowpipe analysis.

Analytical Reactions. — Ammonium salts are generally soluble. H_2PtCl_6 precipitates the double chloride $(\text{NH}_4)_2\text{PtCl}_6$, similar in appearance and crystalline form to the corresponding potassium salt (Plate I, Fig. 2).

Ammonium salts are most easily detected by the evolution

* Dr. Percy Howe in *Dental Cosmos*, Jan. 1912.

of ammonia gas (NH_3) whenever they are heated with fixed alkali, NaOH or KOH .

The test may be made upon the original solution by boiling in a test-tube with a little 10 per cent NaOH , and the escaping NH_3 may be detected by the odor or, better, by suspending in the upper part of the tube a piece of *moistened red* litmus paper, which is promptly turned blue by the "volatile alkali." The litmus-paper test is more delicate than the odor test. Care should be taken that the paper does not touch the sides of the tube, as it may come in contact with traces of NaOH .

Many ammonium solutions give off NH_3 gas without the aid of any fixed alkali. Common examples are the carbonate, acid carbonate, hydrate, sulphide, and sulph-hydrate.

QUESTIONS ON GROUP VI.

Why use alcohol in the precipitation of ammonium or potassium as double chloride with platinum?

Why are the flame tests preferably made with chlorides of the metals?

Why is ammonia called the volatile alkali, and what are the fixed alkalies from which it is thus distinguished?

Analysis of Groups III, IV, and V.

(When phosphates, borates, or oxalates are present.)

To the filtrate from Group II add NH_4Cl and NH_4OH in slight excess. Heat to boiling and add $(\text{NH}_4)_2\text{S}$ slowly (always keeping the solution at the boiling-point) until precipitation is complete. Filter as rapidly as possible and wash with hot water, adding occasionally a little $(\text{NH}_4)_2\text{S}$.

The filtrate, which may contain the barium and potassium groups, must be concentrated by evaporation, filtered if necessary, and set aside.* The precipitate may contain MnS , ZnS , CoS , NiS , FeS , $\text{Al}(\text{OH})_3$, and $\text{Cr}(\text{OH})_3$ with phosphates or oxalates soluble in acids only. The color of the precipitate

* If Ni is present, the filtrate is frequently brown or black, since NiS is somewhat soluble in an excess of $(\text{NH}_4)_2\text{S}$, especially if much NH_4OH is present. The NiS may be precipitated, after evaporation, by acidifying with HCl .

will give some indication of what is present. Test the precipitate for Mn by fusing a part with KNO_3 and Na_2CO_3 .

Treat the precipitate with *cold dilute* HCl in which CoS and NiS alone are insoluble. Filter. Treat insoluble residue for Co and Ni according to directions on page 53.

The HCl solution, which may contain Mn, Zn, Fe, Cr, and Al as chlorides, and phosphates and oxalates soluble in acids, and which is green or violet if much Cr is present, is boiled with a few drops of HNO_3 until all the H_2S is expelled.

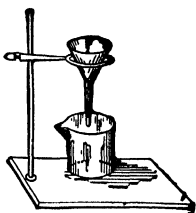
Test a *small* portion of the solution for Fe exactly as in analysis of Group III given on page 48. Of the remainder of the solution take about one-third, and add dilute H_2SO_4 .

A white precipitate may contain BaSO_4 , SrSO_4 , and possibly CaSO_4 . Filter, wash precipitate, and fuse with a mixture of Na_2CO_3 and K_2CO_3 .

Note. — The mixture of the two carbonates in molecular proportions fuses at a lower temperature than either salt alone.

Filter and wash the carbonates thus formed, dissolve them in acetic acid and examine this solution for Ba, Sr, and Ca as directed under the Ba group. To the filtrate from the precipitate produced by H_2SO_4 , or to the solution in which H_2SO_4 has failed to give a precipitate, add three times its volume of alcohol; Ca, if present, is precipitated as white CaSO_4 , and its presence may be confirmed by dissolving the precipitate in water and adding $(\text{NH}_4)_2\text{C}_2\text{O}_4$, which precipitates CaC_2O_4 , white.

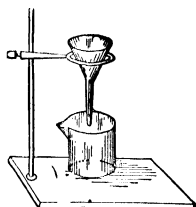
To the rest of the HCl solution add ferric chloride, carefully, till a drop of the solution gives, when mixed with a drop of ammoniac hydrate, a yellowish precipitate. To the solution add Na_2CO_3 or K_2CO_3 till the acid is nearly neutralized, then add excess of freshly precipitated BaCO_3 , and allow to stand over night. Filter.



Cr and Al as hydrates. (Fe as phosphate or hydrate and BaCO_3 .)

MnCl_2 , ZnCl_2 , and possibly members of Group V.

Transfer the precipitate to a small beaker and boil for some time with NaOH or KOH. The Al will be converted into the aluminate KAlO_2 . The phosphate will be more or less completely changed to potassium or sodium phosphate. Filter.



$\text{Cr}(\text{OH})_3, \text{BaCO}_3$, etc.

KAlO_2 and Na_2HPO_4 .

Test precipitate for Cr as on page 48. Add HNO_3 to filtrate till acid, then divide into two parts; test one for P_2O_5 with $(\text{NH}_4)_2\text{MoO}_4$.

Test the other for Al by adding NH_4OH till alkaline; precipitate will then be AlPO_4 , insoluble in acetic acid.

To the solution of Mn and Zn chlorides add a little HCl and boil. Then make alkaline with NH_4OH , add $(\text{NH}_4)_2\text{S}$, warm

OUTLINE SCHEME FOR ANALYSIS OF GROUPS III, IV, AND V.

(Phosphates, oxalates, borates, etc., being present.)

To filtrate from Group II add NH_4Cl and NH_4OH . Heat and add $(\text{NH}_4)_2\text{S}$. Filter rapidly.

Precipitate = $\text{MnS}, \text{ZnS}, \text{CoS}, \text{NiS}, \text{FeS}, \text{Al}(\text{OH})_3, \text{Cr}(\text{OH})_3$, also phosphates, etc., soluble in acids only. Fuse part of precipitate and test for Mn (page 50). Treat remainder w cold dilute HCl.

Filtrate, members of Ba and K groups

Residue = CoS and NiS . Make borax-bead test and separate Co if necessary, w KNO_3 (page 53).

Solution = Mn, Zn, Cr, and Al. Divide solution into three parts of about $\frac{1}{3}$, $\frac{1}{3}$, and $\frac{1}{3}$, respectively, and treat as follows:

I. Test small portion for Fe (page 48).	II. To second portion add dilute H_2SO_4 .		III. To third portion add FeCl_3 to combine w H_3PO_4 , etc., then add Na_2CO_3 or K_2CO_3 , and BaCO_3 (page 72).	
	<i>Precipitate</i> may be BaSO_4 , SrSO_4 or CaSO_4 . Filter, wash, fuse w Na_2CO_3 and K_2CO_3 . Dissolve fusion in HA and analyze for Group V.	<i>Solution</i> = CaSO_4 . Add alcohol; if precipitate occurs, filter, dissolve in H_2O , and test with ammonium oxalate.	<i>Precipitate</i> = Cr, Al, Fe, and BaCO_3 . Boil precipitate w NaOH and filter.	<i>Solution</i> = Mn and Zn. Reprecipitate Mn and Zn as sulphides, and test according to page 53.
			<i>Residue</i> = Cr, BaCO_3 , etc. Test for Cr as on page 48.	<i>Solution</i> = KAlO_2 . Test for Al as on page 48

slightly and filter. The precipitate (MnS and ZnS) may be dissolved in cold dilute HCl and tested for Mn and Zn as in analysis of Group IV, page 53.

ANALYTICAL REACTIONS OF THE ACIDS.

In the analytical processes thus far described, we have considered only the separation and detection of the basic or metallic part of the salt (positive ions); that is, we have analyzed a solution of ferric chloride, and found the iron only. It is necessary also to find the chlorine (negative ion). Before making any examination for negative ions, it will be possible to save a considerable amount of both time and labor by first carefully considering what acids are capable of forming soluble salts with the bases which have already been detected. To facilitate this consideration a table of solubilities is given below, by a careful study of which it will be possible to select such acids as are most likely to be present in the unknown solution under investigation, and also to neglect a number of acids which, from the solubility of their salts, together with the character of the solution (acid, alkaline, neutral and aqueous, or otherwise), will necessarily be absent.

TABLE SHOWING THE SOLUBILITY OF SALTS

	K	Na	NH ₄	Mg	Ba	Sr	Ca	Mn	Zn	Co	Ni	Fe	Fe ₂
Acetate.....	w	w	w	w	w	w	w	w	w	w	w	w	w
Arsenate.....	w	w	w	a	a	a	a	a	a	a	a	a	a
Arsenite.....	w	w	w	a	wa	wa	a	a	a	a	a	a	a
Borate.....	w	w	w	wa	a	a	a	a	a	a	a	a	a
Bromide.....	w	w	w	w	w	w	w	w	w	w	w	w	w
Carbonate.....	w	w	w	a	a	a	a	a	a	a	a	a	a
Chlorate.....	w	w	w	w	w	w	w	w	w	w	w	w	w
Chloride.....	w	w	w	w	w	w	w	w	w	w	w	w	w
Chromate.....	w	w	w	w	a	wa	wa	w	w	a	a	w	w
Cyanide.....	w	w	w	w	wa	w	w	a	a	ai	ai	ai	
Iodide.....	w	w	w	w	w	w	w	w	w	w	w	w	w
Nitrate.....	w	w	w	w	w	w	w	w	w	w	w	w	w
Oxalate.....	w	w	w	a	a	a	a	a	a	a	a	a	a
Oxide.....	w	w		a	w	w	w	a	a	a	a	a	a
Phosphate.....	w	w	w	a	a	a	a	a	a	a	a	a	a
Silicate.....	w	w		a	a	a	a	a	a	a	a	a	a
Sulphate.....	w	w	w	w	i	i	wi	w	w	w	w	w	w
Sulphide.....	w	w	w	wa	w	w	w	a	a	a	a	a	a
Sulphocyanate.....	w	w	w	w	w	w	w	w	w	w	w	w	w
Tartrate.....	w	w	w	wa	a	a	a	wa	a	w	a	wa	w

TABLE SHOWING THE SOLUBILITY OF SALTS. — CONCLUDED.

	Cr ₂	Al ₂	Sb	Sn''	Sn ^{IV}	Au	Ag	Hg ₂	Hg	Pb	Bi	Cu	Cd
Acetate.....	w	w	w	w	w		wa	wa	w	w	w	w	w
Arsenate.....	a	a	a	a	a		a	a	a	a	a	a	a
Arsenite.....			a	a	a		a	a	a	a	a	a	a
Borate.....	a	a		a			a			a	a	a	wa
Bromide.....	w	w	wa	w	w	w	i	ai	wa	wi	wa	w	w
Carbonate.....							a	a	a	a	a	a	a
Chlorate.....	w	w		w			w	w	w	w	w	w	w
Chloride.....	w & i		wa	w	w	w	i	ai	w	wi	wa	w	w
Chromate.....	a		a	a			a	a	wa	ai	a	w	a
Cyanide.....	a					w	i		w	a	wa	a	a
Iodide.....	w	w	wa	w	w	a	i	a	a	wa	a	a	w
Nitrate.....	w	w		a	a		w	w	w	w	a	w	w
Oxalate.....	w	a	a	a	w		a	a	a	a	a	a	a
Oxide.....	a & i	a & i		a	a & i		a	a	a	a	a	a	a
Phosphate.....	a	a	a	a	a		a	a	a	a	a	a	a
Silicate.....	a	ai										a	a
Sulphate.....	w & a	w	a	w	w		wa	wa	wa	i	a	w	w
Sulphide.....			a	a	a	a	a	a	a	a	a	a	a
Sulphocyanate.....	w				w		i	a	w	a	a	a	wa
Tartrate.....		w	w	wa			a	a	a	a	a	wa	wa

w, soluble in water; a, insoluble in water, soluble in acids; i, insoluble in water or acids; wa, sparingly soluble in water, readily soluble in acids; wi, sparingly soluble in water and acids; ai, sparingly soluble in acids only.

In this connection it is well to remember that practically all nitrates and chlorates are soluble in water; sulphates are mostly soluble, except those of barium, strontium, and calcium. Phosphates (di- or trimetallic), silicates, oxalates, and borates are practically insoluble, except those of the alkaline metals. This latter statement is also true of carbonates, except that some of the carbonates will dissolve to an appreciable extent in water containing carbon dioxide. Nearly all chlorides, bromides, and iodides, except those of the first-group metals, are soluble. Sulphides are insoluble, except those of Groups V and VI. Acid salts are usually more soluble than neutral salts.

In making qualitative tests for the negative ions, it is not necessary to separate them one from the other, as it is in the case of metals; hence the tests are individual ones, usually made upon the original substance or solution, and often require confirmation before conclusive evidence is obtained. The grouping is, therefore, simply for convenience, as it thus becomes possible to exclude a considerable number of acids by a single general test.

ACID GROUPS (NEGATIVE IONS).

Group I may include such acids as give effervescence when their dry salts are treated with *dilute* H_2SO_4 , as H_2CO_3 , H_2S , $\text{H}_2\text{S}_2\text{O}_3$, H_2SO_3 , and HCN .

Group II may include acids giving a precipitate with AgNO_3 in dilute HNO_3 solution, as HCl , HBr , HI , HCN , HCNS , HNO_2 , HClO , $\text{H}_4\text{Fe}(\text{CN})_6$, $\text{H}_3\text{Fe}(\text{CN})_6$, $\text{H}_2\text{S}_2\text{O}_3$, H_2S and $\text{H}_2\text{P}_2\text{O}_7$.

This second group may be further subdivided into three parts, according to the color of the precipitate obtained (pages 78 and 80).

Group III may include acids forming insoluble salts with BaCl_2 or CaCl_2 and not found in Groups I or II, as H_2SO_4 , $\text{H}_2\text{C}_2\text{O}_4$, H_3PO_4 , H_3BO_3 , H_2CrO_4 and H_2SiO_3 .

Group IV: We may put in Group IV any acids not included in the foregoing groups. Of common occurrence are nitric (nitrates), chloric (chlorates), and acetic (acetates).

DETECTION OF ACIDS OF GROUP I.

(Acids effervescing with dilute sulphuric acid. H_2CO_3 , H_2S , H_2SO_3 , $\text{H}_2\text{S}_2\text{O}_3$, HCN .)

To a test-tube, one-quarter full of the unknown solution, or a little dry substance on a watch-glass, add dilute H_2SO_4 . If solution is very dilute, concentrate it before making test, as a slight amount of gas might be absorbed by the water. Watch carefully for any escape of gas and note any odor which may be given off.

Carbonates evolve CO_2 , odorless, but if passed into lime-water or baryta-water will give white precipitate of CaCO_3 or BaCO_3 .

Sulphides evolve H_2S , odor of rotten eggs. Confirm by adding a little dilute H_2SO_4 to the suspected powder (or solution) in a test-tube and holding over the mouth of the tube a piece of filter-paper wet with a solution of lead acetate. The test-tube may be warmed slightly to expel the gas; a dark-colored stain, due to the formation of PbS will then appear on the filter-paper.

Sulphites evolve SO_2 , odor of burning sulphur. Sulphites in *neutral* solution may be further identified by the deep-red

color produced with ferric chloride. The color is discharged upon addition of dilute acids, HCl, or H_2SO_4 (differing from HCNS).

Thiosulphates also evolve SO_2 , but at the same time the mixture becomes cloudy from precipitation of sulphur.*

Thiosulphates in neutral solution treated with ferric chloride give a violet to purple color, fading (rapidly upon warming) to a colorless solution. In mixtures of sulphites and thiosulphates both acids may often be detected by the use of FeCl_3 , the deep-red coloration of the mixed acids rapidly fading to the lighter red of $\text{Fe}_2(\text{SO}_3)_3$ (not to colorless solution).

Cyanides evolve HCN, odor of peach-stones. (Mercuric cyanide does not respond to this reaction.) Confirm by reactions given under Group II.

PRELIMINARY TESTS FOR COMMON ACIDS OF GROUPS II AND III.

(In preparatory courses the acids given in this list may be sufficient.)

From the acids of Group II and III it may be desirable to select for laboratory practice, at least at the beginning of the acid work, the more common members of the groups. These will be HCl, HBr, HI, HCN, and H_2S of Group II and H_2SO_4 , $\text{H}_2\text{C}_2\text{O}_4$, and H_3PO_4 of Group III; and tests for them may be made as follows:

Chlorides give with AgNO_3 in presence of HNO_3 a white curdy precipitate of AgCl, much more freely soluble in ammonia than any other acid of the group here given except the cyanide AgCN; but HCN is a member of the *first* acid group and would have been previously detected.

Bromides with AgNO_3 and HNO_3 give a precipitate of AgBr similar in appearance to AgCl, but with a slightly yellowish color and only sparingly soluble in NH_4OH .

The tests, described on page 80, should also be made if bromides and iodides are suspected in the solution.

* Sulphides may also precipitate sulphur in presence of compounds capable of oxidizing the H_2S , such as FeCl_3 . In the absence of sulphates either H_2SO_3 or $\text{H}_2\text{S}_2\text{O}_3$ can be oxidized to H_2SO_4 by heating with HNO_3 and a precipitate of BaSO_4 obtained with BaCl_2 .

Cyanides, see Group I.

Sulphides will give a black precipitate with AgNO_3 , and have been previously considered in Group I.

Sulphates may be detected by first acidifying the solution strongly with HCl (filtering out a precipitate if any occurs) and adding a solution of BaCl_2 ; a white precipitate will then be BaSO_4 , showing presence of sulphates in solution tested.

Phosphates in a solution containing HNO_3 and free or nearly free from HCl will give, with ammonium molybdate, a yellow crystalline precipitate of ammonium phosphomolybdate.

Oxalates may be detected, in a solution free from sulphates and which is slightly acid with acetic acid, by simple addition of calcium chloride, which will precipitate CaC_2O_4 , white and crystalline.

DETECTION OF ACIDS OF GROUP II.

(Giving precipitate with AgNO_2 in presence of dilute HNO_3 .)

To the solution to be tested add a *very* slight amount of HNO_3 and a few cubic centimeters of AgNO_3 solution. A precipitate indicates acids of this group.

(A) If the precipitate is *white*, the presence of chlorides (HCl), cyanides (HCN), sulphocyanates (HCNS), ferrocyanates (H_4FeCy_6), hypochlorites (HClO),* or nitrites (HNO_2) is indicated.

To separate or identify these silver precipitates, allow to settle, decant the supernatant fluid, and add NH_4OH . Shake thoroughly; the chloride (AgCl), cyanide (AgCN), and nitrite (AgNO_2) will then dissolve easily, the sulphocyanate (AgCNS) and the ferrocyanide ($\text{Ag}_4\text{Fe}(\text{CN})_6$) slowly or slightly.

If HCNS , or $\text{H}_4\text{Fe}(\text{CN})_6$ is indicated, test original solution with a few drops of FeCl_3 . Sulphocyanates or thiocyanates (HCNS) give a deep blood-red solution. The color is soluble in ether and may be discharged by HgCl_2 . Ferrocyanides ($\text{H}_4\text{Fe}(\text{CN})_6$) give a deep-blue precipitate. (See page 45.)

* Precipitate is AgCl . Reaction is $3 \text{NaClO} + 3 \text{AgNO}_3 = 2 \text{AgCl} + \text{AgClO}_3 + 3 \text{NaNO}_3$.

Acids forming white silver precipitates, easily soluble in ammonia, may be distinguished as follows:

Chlorides (HCl) may be distinguished from HBr and HI by the ready solubility of the silver precipitate in NH_4OH . If bromides and iodides are present, liberate the halogens by means of MnO_2 and H_2SO_4 and pass the mixed gases into a solution of aniline in acetic acid (4 c.c. of saturated aqueous solution of aniline and 1 c.c. glacial acetic acid). Iodine gives no precipitate, bromine gives a white one and chlorine a black one. (Prescott and Johnson's "Qualitative Chemical Analysis," page 336.)

This is a delicate and very satisfactory test for bromine but not so delicate for chlorine in the presence of bromides. For such cases the following *chloro-chromic anhydride test* is recommended. Neutralize the solution if necessary, evaporate to dryness, transfer residue to a test-tube of rather small diameter, add a little solid $\text{K}_2\text{Cr}_2\text{O}_7$, then concentrated H_2SO_4 . Decant the *fumes* into a wider test-tube containing a few cubic centimeters of NH_4OH .

If the chloro-chromic anhydride is evolved, ammonium chromate will be formed. Test by making acid with acetic acid, then adding acetate of lead. A yellow precipitate of lead chromate indicates chlorine in the original solution.

Hypochlorites liberate I from KI without the addition of acid.

Note. — Hypochlorite solutions are usually quite strongly alkaline, and in such cases a considerable amount of iodide is necessary to obtain the characteristic color in chloroform or with starch.

Nitrites liberate I from KI after the addition of acetic acid. They also give a brown coloration with acetic acid and a crystal of ferrous sulphate. (Nitrates require a stronger acid.)

Note. — This test is much more delicate than either of the others given, and if the solution is very dilute it is well to make it, even if the indigo color is not discharged.

Further mix a little of the solution with a few cubic centimeters of dilute indigo solution and shake. The indigo is decolorized either by hypochlorites (HClO) or by nitrites (HNO_2).

Cyanides may be tested for as under Group I. If this test is not conclusive, they may be converted into sulphocyanides by

the addition of a few drops of $(\text{NH}_4)_2\text{S}$ and evaporation on the water-bath to dryness. They may then be dissolved in a little distilled H_2O , filtered and tested with FeCl_3 .

(B) The precipitate is red-brown or orange, soluble in $\text{NH}_4\text{OH} = \text{H}_3\text{Fe}(\text{CN})_6$. *Ferricyanide* indicated.

(C) The precipitate is black or turns black upon warming: H_2S turns black immediately. HH_2PO_2 starts to precipitate white, but rapidly turns black, $\text{H}_2\text{S}_2\text{O}_3$ precipitates white and turns black slowly or upon heating.

Sulphides (H_2S) and *thiosulphates* ($\text{H}_2\text{S}_2\text{O}_3$) may also be detected as described under Group I, Acids.

(D) If the precipitate, originally obtained, is yellow and insoluble in NH_4OH , *iodides* are indicated; if yellowish white and slowly soluble in NH_4OH , *bromides* are probably present.

Iodides and *bromides* (HI and HBr) may be detected in the same solution by adding chlorine water, very cautiously at first, and shaking with chloroform. The chlorine liberates the iodine, which is dissolved by the chloroform with violet color. Excess of chlorine decolorizes the iodine and liberates the bromine which, in turn, is dissolved by the chloroform with yellow to red color.

ACIDS OF GROUP III.

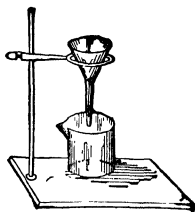
(Acids forming insoluble barium or calcium salts, not included in the Acid Group I or II.)

The members of this group may be separated from each other, although this is not necessary unless several members are present. H_2SO_4 , $\text{H}_2\text{C}_2\text{O}_4$, H_2CrO_4 , H_2SiO_3 , H_3BO_3 , H_3PO_4 , separated as follows: To a little of the unknown solution add 2 or 3 c.c. of HCl ; a white or gelatinous precipitate which is not dissolved by dilution with water and warming is probably silicic acid. Make a bead test with microcosmic salt; the particles of SiO_2 remain undisturbed by the hot bead, forming the so-called silicon "skeleton." Filter out the silicic acid and add CaCl_2 or a mixture of BaCl_2 and CaCl_2 ; a white precipitate will be BaSO_4^* (test for *sulphates*),

* If the HCl is too strong, BaCl_2 may be precipitated as such, but the precipitate in this case will form more slowly than the BaSO_4 ; it will have a crystalline appearance and will dissolve upon addition of water.

the Ba and Ca salts of all remaining acids of the group being soluble in HCl.

Filter out the BaSO_4 , and to the filtrate add NH_4OH , which will cause a precipitate of barium *oxalate*, *chromate*, *borate*, and *phosphate*. Filter, wash precipitate two or three times, reject wash-water, then transfer to test-tube by making a small hole in point of paper and forcibly washing through with the least possible amount of water; acidulate strongly with acetic acid, which will dissolve the phosphates and borates, leaving undissolved the oxalates (BaC_2O_4 , white) and chromates (BaCrO_4 , yellow).



Oxalic and chromic acids as barium salts.

Phosphoric and boric acids.

Divide the filtrate into two parts, (a) and (b). Test one part, (a), for H_3PO_4 by adding to it an excess of ammonium molybdate* (in HNO_3), when a yellow precipitate (forming sometimes after several hours' standing) is ammonium phosphomolybdate (test for *phosphates*); the mixture may be warmed to hasten precipitation; the degree of heat should not exceed 40°C ., as the ammonium molybdate might be decomposed, giving a yellow precipitate similar to the phosphomolybdate.

Note. — If As is present, it must be removed by H_2S before testing for H_3PO_4 .

Test the other part, (b), for H_3BO_3 by evaporating to dryness in a porcelain dish; then moisten with strong H_2SO_4 , cover with a little alcohol, and ignite. Boric acid will give the flame (particularly the edge) of the burning alcohol a green color due to formation of ethyl borate. This color is more easily apparent if the dish is placed in a darkened corner.

A test for H_3BO_3 may also be made with turmeric paper, which, if dipped into a solution of boric acid, or of a borate mixed with HCl or H_2SO_4 to slight but distinct acid reaction, and dried at 100° , becomes red; the red color becomes bluish-black or

* Preparation of ammonium molybdate solution, appendix, page 176.

greenish-black when moistened with a solution of an alkali or an alkaline carbonate. If there is a suspicion that H_2CrO_4 and $\text{H}_2\text{C}_2\text{O}_4$ are both present, dissolve the precipitate of barium oxalate and chromate off the paper with dilute HCl ; divide the filtrate into two parts and test one for H_2CrO_4 by addition of H_2O_2 , which with chromates in presence of HCl produces a deep-blue solution and ultimately CrCl_3 .

In the *absence* of chromates, the precipitate being white, oxalates may be confirmed by coloring the second part of the solution a faint pink with a dilute solution of KMnO_4 and warming, when the color will be discharged.

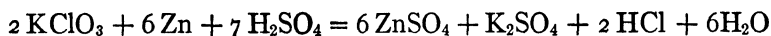
In the *presence* of chromates, the precipitate being yellow, it will be necessary to test the original solution for oxalates as follows: To a few centimeters of the unknown add alcohol; warm. The chromate will be reduced to CrCl_3 . Add NH_4OH till alkaline and filter out the precipitate, $\text{Cr}(\text{OH})_3$. The filtrate may be tested for oxalic acid as above, or with CaCl_2 , a white precipitate being CaC_2O_4 .

ACIDS OF GROUP IV.

The remaining acids of importance not included in either of the three preceding groups are nitric, HNO_3 , chloric, HClO_3 , and acetic, $\text{HC}_2\text{H}_3\text{O}_2$.

Nitrates. — Saturate 5 c.c. of a very dilute nitrate solution with FeSO_4 . Filter and carefully underlay the clear filtrate with concentrated sulphuric acid; a dark ring (pale red-brown to nearly black) at a point of contact of the two liquids shows presence of a nitrate.

Chlorates. — A solution free from chlorides or hypochlorites, treated with Zn and dilute H_2SO_4 , will give a test for HCl if chlorates were originally present, the chlorate having been reduced by the nascent hydrogen:



Boiling with sulphurous acid also reduces HClO_3 (and HClO) to HCl .

If the substance is in solid form, a *very small particle* may be warmed with concentrated H_2SO_4 . Chlorates detonate and give off yellow fumes of ClO_2 :



Acetates with ferric chloride give a red color which is not discharged by HgCl_2 (differing from sulphocyanate), but may be discharged by HCl (differing from sulphocyanate and meconate).

A more positive test is the formation of the ethyl ester or acetic ether. A blank test for comparison should always be made, the method of procedure being as follows:

Take two test-tubes of practically equal diameter, mix in each equal volumes of alcohol and strong sulphuric acid; warm the tubes together; then into one introduce a few centimeters of the unknown solution, and into the other an equal volume of water. Heat again to a boiling-point and compare the odors from the two tubes. The acetate is easily detected if present.

CHAPTER III.

ANALYSIS IN THE DRY WAY.

In the examination of solid substances, much may be learned by a few simple tests directly applied to the substance, which has been reduced (if necessary) to the form of a powder.

Some of these are generally used as preliminary to the solution of the substance and regular analysis in the wet way. These tests may be made quickly, and, with a little elaboration, will often give all the information required regarding an unknown substance.

The practical questions of actual experience are usually simple ones. It is not an analysis of an unknown solution possibly containing all the metals of one or more groups that interests an active practitioner, but a specific inquiry as to whether or not this or that preparation contains or does not contain the necessary or the undesirable ingredient, whether the thing is of the composition or of the strength represented. A few minutes' work in the laboratory, especially if aided by the microscopical tests given in a subsequent chapter, will frequently be found sufficient to answer questions of this character.

The tests made in the dry way are not as delicate, nor are the results obtained (especially negative ones) as conclusive, as those of a systematic analysis of the substance in solution, and in occasional cases it may be necessary to resort to the more tedious process.

Before undertaking the analysis of a substance, note carefully its physical properties of odor, color, and solubility; also whether it is magnetic, metallic, or crystalline.

The volatile acids, certain ammonium compounds, bromine, and iodine may frequently be detected by their odor.

COLORS OF SALTS AND SOLUTIONS.

The following colored salts are *soluble* in water:

Black	Silver albuminate (argyrol, etc.).
Violet or purple	Chromic salts and permanganates.
Red	{ CrO_3 and acid chromates, $\text{K}_3\text{Fe}(\text{CN})_6$, sodium-nitro-prusside, H_2PtCl_6 .
Reddish-brown or purple-red	Manganic salts.
Reddish-yellow	Ferric salts and AuCl_3 .
Yellow	{ Neutral chromates of the alkalis, salts of uranium.
Pale yellow	$\text{K}_4\text{Fe}(\text{CN})_6$ (Potassium ferrocyanide).
Pink	Salts of cobalt.
Pale pink	Manganous salts.
Green	{ Ferrous salts, nickel salts, certain copper salts.
Dark green	Some chromic salts.
Bluc-green	Chromates.
Blue	Cupric salts.

The following colored substances are *insoluble* in water:

Black	{ Carbon and carbides, metals, many metallic sulphides, oxides of Cu, Fe, Mn, and Pb. Iodine is bluish black.
Red	HgO , HgS , HgI_2 , Pb_3O_4 , As_2S_2 .
Brick-red	Amorphous phosphorus, Fe_2O_3 .
Light brown	PbO (litharge).
Yellow	{ S, HgO , CdS , As_2S_3 , PbI_2 , Ag_3PO_4 , ammonium phosphomolybdate, and chromates of the heavy metals, PbCrO_4 , BaCrO_4 .
Green	{ Some copper compounds, Cu_2I_2 , Paris green, etc., Cr_2O_3 .
Blue	{ Some copper compounds, Prussian blue, ultramarine; anhydrous salts of cobalt.

METHODS OF EXAMINATION.

Powder the substance and apply tests described in this chapter, which will be considered in the following order:

- A. Ignition with free access of air.
- B. Closed-tube test.
- C. Flame test on platinum wire.
- D. Examination with the blow-pipe on plaster slab.

- E. Examination with blowpipe on charcoal.
- F. Bead tests on platinum wire.
- G. Special tests, distinguishing or confirmatory.

A. IGNITION IN AIR.

This test may be made on a crucible cover or on platinum foil. If there is any probability of I, Br, Cl, P, or easily reduced metallic compounds in the unknown substance, the platinum foil is likely to be destroyed: hence, the porcelain is recommended.

The heat employed should be very low at first; then it should be gradually increased and the test carefully watched.

The majority of phenomena occurring under A are more easily observed in the test made with closed tube, B, and will be given under that head.

OBSERVED PHENOMENA.

The substance *melts* and steam is given off.

The substance *burns* (a) at comparatively low temperature with blue flame and odor of SO₂ or burning matches.

- (b) With yellow flame and much smoke.
- (c) Blackens and then burns at fairly high temperature, leaving white or gray ash.
- (d) Blackens without burning.

Vapors are given off:

- (a) Of a violet color.
- (b) Of a red-brown color.
- (c) Of a greenish-yellow color
- (d) White, practically odorless.
- (e) White with odor of NH₃.
- (f) White with odor of garlic.
- (g) White and yellow with ammoniacal or empyreumatic odor.

The substance decrepitates.

Examine residue on foil (porcelain); add a drop or two of water and test with litmus-paper.

If found to be acid.

If alkaline without blackening.

If alkaline with blackening.

Add a drop of dilute HCl, effervescence.

INDICATIONS.

Water of crystallization.
NN₄NO₃ or H₂C₂O₄, which entirely disappears.
Sulphur.

Fat, waxec, resins, etc.
Carbonaceous matter other than fats, etc.
Formation of oxides of Fe, Co, Ni, or Cu.

Iodine.
Br or nitrogen oxides.
Chlorine or ClO₂.
Some ammonium salts, NH₄Cl, (NH₄)₂SO₄, etc.
Ammonium carbonate.
Arsenic.
Organic matter.

Water held mechanically by crystals, as NaCl, etc.

Acid salts.
Fixed alkali hydrates or carbonates.
Carbonate formed by combustion of organic compounds.
Carbonates.

PLATE II. — SUBLIMATES.

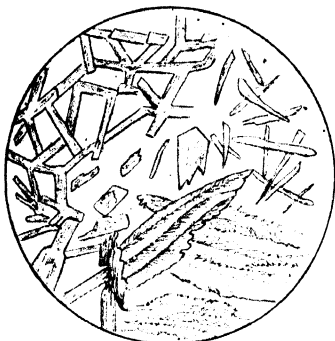


FIG. 1.
Oxalic Acid (Sublimed).

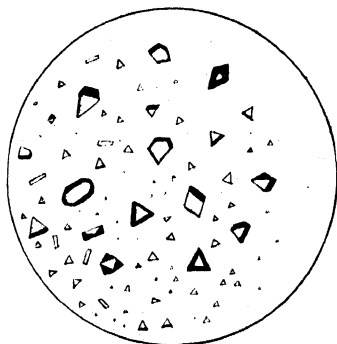


FIG. 2.
Arsenic Trioxide.

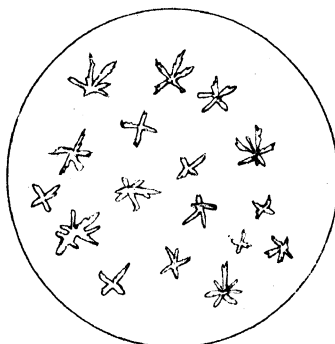


FIG. 3.
Mercuric Chloride (Sublimed).

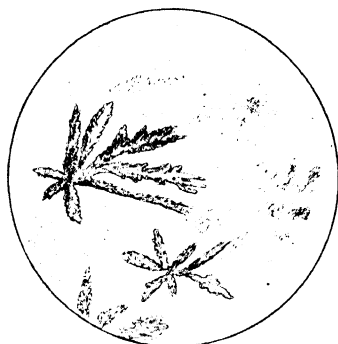


FIG. 4.
Ammonium Sulphate (Sublimed).

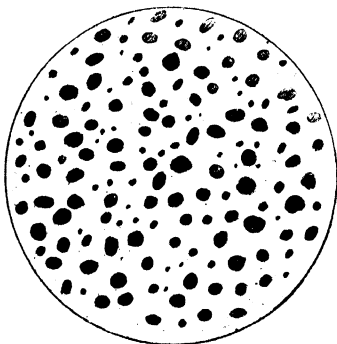


FIG. 5.
Mercury from HgO .

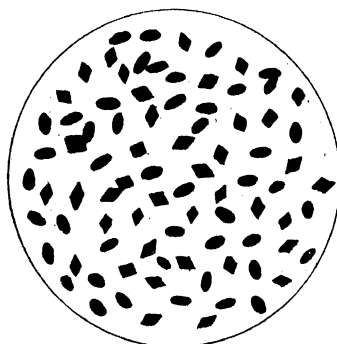


FIG. 6.
Todine.

B. CLOSED-TUBE TEST.

Select a tube of soft glass about 5 or 6 inches in length. Seal one end and enlarge slightly. Into the bulb thus formed introduce a few grains of the unknown powdered substance. Heat carefully, making the following tests at various stages of the process. Note the odor of escaping gases.

OBSERVED PHENOMENA.	INDICATIONS.
STEAM condenses in cold part of tube. OXYGEN is evolved.	See under A. A peroxide, chlorate, some oxides (as HgO), alkali nitrates.
CARBON DIOXIDE is evolved.	Carbonates, oxalates (at high temperature), organic matter.
A COMBUSTIBLE GAS is formed: (a) Burning with a luminous flame; black residue remains in tube. (b) Burning with a blue flame. (c) Burning as in (b) and with odor of SO_2 .	Hydrocarbons from organic matter. CO from oxalates. H_2S from moist sulphides.
A SUBLIMATE FORMS in the cooler part of the tube. Examine under microscope. Colorless with partial decomposition. Color is <i>white</i> with production of garlic odor, crystalline. Color is <i>white</i> when cold. Yellow when hot, crystalline. Color is <i>white</i> — it sublimes directly without melting and blackens with NH_4OH . A white sublimate which by treatment with slaked lime yields NH_3 . A white sublimate of As_2O_3 with black residue in tube and odor of acetic acid. Sublimate is gray, consisting of small globules which can be made to unite by rubbing. Sublimate consists of reddish-yellow to red globules, yellow when cold. Sublimate darker than above and reddish-yellow when cold. Sublimate is brown to black "metallic mirror," soluble in NaClO . Ditto; dead black, insoluble in NaClO . Sublimate is black accompanied by violet vapor. Sublimate black, turning red when rubbed. No sublimate is formed, but the COLOR CHANGES to Yellow when hot, white when cold. Reddish-brown when hot, yellow when cold. Black when hot, red when cold. Black when hot, brick-red when cold. Dark orange when hot, yellow when cold.	Oxalic acid. Plate II, Fig. 1. As_2O_3 . Plate II, Fig. 2. HgCl_2 . Plate II, Fig. 3. HgCl . Ammonium salts. Plate II, Fig. 4. Paris green. Hg from HgO , amalgam, etc. Plate II, Fig. 5. Sulphur. Native sulphide of arsenic. Metallic arsenic. Metallic antimony. Iodine. Plate II, Fig. 6. HgS , cinnabar.
BLACK RESIDUE without other visible manifestation.	ZnO . PbO or Bi_2O_3 . (See D.) HgO (Hg sublimes). Fe_2O_3 . Chromates of Pb, etc. Oxides of Cu, Co, etc. (See A.)
SUBSTANCE MELTS without a sublimate being formed.	Salts of the alkaline metals.

Test for oxygen by inserting a glowing splinter into the tube.

Test for combustible gases by occasionally applying flame to the open end of the tube.

Bring to the mouth of the tube a clear drop of $\text{Ba}(\text{OH})_2$ solution. If the drop becomes turbid, CO_2 is indicated.

C. FLAME TEST WITH PLATINUM WIRE.

Introduce the substance on platinum wire into the edge of the flame. More satisfactory results are sometimes obtained if the solid is first moistened with HCl (page 64, note). The flame is colored as follows: by Na, yellow; K, violet; Ni, carmine; Sr, crimson; Ca, orange-red; Ba, yellowish green; Cu, usually bright green; CuCl_2 , an intense blue; H_3BO_3 , pale green; Sb, greenish blue; Pb, As, Bi, livid blue.

D. BLOWPIPE TEST ON PLASTER.*

(Use oxidizing flame.)

Smooth plaster slabs, about 1 inch wide and 4 inches long, are well suited for these tests. These may be prepared by making a magma of calcined plaster and pouring upon a glass plate. Before it hardens, mark deeply with a spatula into slabs of desired shape and, after it is thoroughly dried, break as marked.

Make a little depression near one end of the slab and in it place a small amount of the substance to be tested; then if a fine oxidizing flame is made to play over the *surface* of the assay, characteristic coatings of oxide or sublimate may be obtained.

In many cases the character of the substance may be determined more easily by first moistening the assay with various reagents. Tetrachloride of tin, cobalt nitrate, and "sulphur iodide" are the most valuable of the reagents so used. The "sulphur iodide" is not of definite composition, but a mixture of about equal weights of sulphur and potassium iodide.

* Substances sufficiently identified by previous tests have been omitted. This method will be found useful mainly in the identification of metals.

The author was greatly aided in the preparation of this list by Mr. Geo. F. S. Pearce of the Harvard Dental School, who carefully verified each test.

D. I. *Examination without Reagents.*

OBSERVED PHENOMENA.	INDICATIONS.
Substance melts to bright metallic globules with brownish-yellow deposit near assay. Requires high heat. Assay revolves.	Silver.
Substance melts to bright globule with coating on plaster, deep orange when hot, light yellow when cold.	Lead or bismuth. (See D. II.)
Substance remains or becomes black without melting. No coating on plaster.	Copper or iron. (See A; also F.)
Substance volatilizes with white fumes, but leaves dark stain; gray to black.	Antimony or arsenic. (See G.)
Substance melts with white or gray oxide on assay.	Tin. (See D. III.)
Forms a white or gray oxide <i>without</i> fusion. Coating on plaster is yellow over brownish-black.	Cadmium.
Forms bulky white oxide with active combustion of assay.	Magnesium.
Forms gray coating easily volatilized.	Mercury from amalgams. (See D. II.)
Cherry-red — crimson to black according to amount of substance deposited. Odor of rotten horse-radish; coating not permanent.	Selenium.
White coating or white fumes at very high heat. Assay burns with bluish-white light.	Zinc. (See D. III.)
Silver-white. Assay remains unchanged.	Platinum, metallic.

D. II. *Cover Substance with KI and S. Use Oxidizing Flame.*

OBSERVED PHENOMENA.	INDICATIONS.
Dirty-white and light-gray coating. Treated with fumes of strong NH_3 and again placed in oxidizing flame, gives bright-red color. Metallic globule is dull and brittle.	Bismuth.
Dirty-white half an inch from assay. Brown directly under assay. No change when treated as above with strong ammonia fumes. Metallic globule is bright and malleable.	Lead.
No coating near assay. Lead-colored, one to one and a half inches, shading to yellow.	Mercury.
Coating bright red when hot, fading to yellow when cold.	Cadmium.
Fine brown coating, very volatile.	Antimony.

D. III. *Examination with Solution of Cobalt Nitrate.*

Heat substance on plaster in the oxidizing flame, moisten well with cobalt nitrate, and again apply oxidizing flame.

OBSERVED PHENOMENA.	INDICATIONS.
Color is deep blue.	Aluminium.
Substance is infusible.	Infusible silicates. (See F.)
Color is fine blue. Substance fusible.	Alkaline silicate, borate, or phosphate.
Color is yellowish-green.	Zinc.
Drab to bluish-green.	Tin.

ANALYSIS IN THE DRY WAY

D. IV. *Examination with Tetrachloride of Tin.*

OBSERVED PHENOMENA.	INDICATIONS.
Changing pale blue to lavender.	Bismuth.
Changing fine blue, in places almost black.	Antimony.
Delicate pink to red produced only by oxidizing flame.	Neutral and acid chromates.

E. BLOWPIPE TESTS WITH CHARCOAL

(Use reducing flame)

Evolution of SO_2 generally indicates a sulphide. A garlicky odor indicates the presence of As.

Deflagration indicates the presence of nitrates or chlorates. If the substance melts and is absorbed by the charcoal, salts of the K group are indicated.

If a white residue remains, infusible and luminous, oxides of Na, Sr, Ca, Mg, Al_2 , Zn, or SiO_2 are indicated. Touch the residue with a piece of moist red litmus paper; if it turns blue, oxides of the Ba group are indicated. Moisten the residue, when cold, with a drop of $\text{Co}(\text{NO}_3)_2$ and again heat in the outer flame. If the residue becomes colored, blue indicates Al_2 (also phosphates and silicates); green, Zn; pink, Mg; bluish-green, SnO_2 .

If a colored residue remains, or metallic scales or globules are seen, with or without incrustation on the charcoal, mix a portion of the substance with Na_2CO_3 , and heat on charcoal in the reducing flame.

(1) A metallic globule, without incrustation.

Brilliant white, malleable; indicates Ag.	
Yellow, " " Au.	
Red, " " Cu (flame colored green).	

Pt, Fe, Co, Ni, Mn are reduced but do not fuse. Fe, Co and Ni are attracted by a magnet.

(2) A metallic globule, with incrustation.

GLOBULE.	INCRUSTATION.	INDICATES PRESENCE OF
White; brittle...	Dark-orange when hot; yellow when cold.....	Bi.
White; brittle...	White both hot and cold.....	Sb.
White; malleable: —		
does not mark paper, Faint-yellow when hot; white when cold.....		Sn.
White; malleable; —		
marks paper ..	Orange-yellow when hot; white when cold.....	Pb.

(3) No globule. Metal reduced but instantly volatilized.

Arsenic: White incrustation; garlic odor.

Zinc: Incrustation, yellow while hot, white when cold.

Cadmium: Incrustation, reddish-brown.

The appearances above described may be modified when two or more metals are present: e.g., yellow alloys may be formed when Cu and Sn, or Cu and Zn, are present together.

F. BEAD TESTS.

The bead tests are made with borax, as described on page 49, or in a similar manner with microcosmic salt, $\text{NaNH}_4\text{HPO}_4$, which by action of the heat gives up NH_3 and H_2O , becoming sodium metaphosphate, NaPO_3 . These substances, fused on a loop of platinum wire, unite with many of the metallic oxides, forming "beads" of various characteristic colors, some of the more important being given below.

With Borax.

Co in the oxidizing flame gives an intense blue bead.

Ni gives red-brown, yellow when cold.

Cu gives green, blue, or bluish-green when cold.

Cr gives green.

Fe gives red, yellowish when cold.

Mn gives amethyst.

With Microcosmic Salt.

Cobalt, copper, nickel, and iron give colors similar to those obtained with borax. Manganese gives a violet bead when heated in the oxidizing flame, but a colorless one in the reducing flame.

G. SPECIAL TESTS DISTINCTIVE OR CONFIRMATORY.

The oxides of copper and iron may be distinguished by adding a drop of HNO_3 , warming gently to drive off excess of acid (high heat will decompose the nitrate, giving the oxide again), and then adding a drop of solution of $\text{K}_4\text{Fe}(\text{CN})_6$. Fe will give a dark-blue coloration; Cu will give a brown.

To distinguish between As and Sb stains, add a drop of hypochlorite solution (NaClO). The arsenic stain will dissolve; the antimony stain will remain unaffected (see page 34).

Antimony gives a very characteristic coating on plaster if treated with tetrachloride of tin. The coating is bluish-black near assay, fading away to a very delicate color at greater distance. It appears almost immediately and is permanent.

In case of suspected silicates make the "silica skeleton" with a bead of microcosmic salt (page 80).

CHAPTER IV.

DENTAL METALLURGY.

INCLUDING A DETAILED STUDY OF THE COMMON METALS,
THE PREPARATION AND PROPERTIES OF ALLOYS,
AMALGAMS, SOLDERS AND CEMENTS.

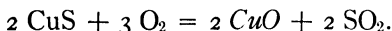
OCCURRENCE OF THE METALS.

The metals occur free in nature to quite an extent, but more often combined with other elements. They are combined chiefly as oxides, sulphides, carbonates and silicates; in one or more of these four forms the great mass of metals contained in the earth's crust are found.

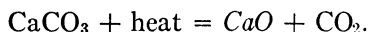
Metallic sulphates are found to a considerable extent.

Other natural sources of the metals are phosphates and chlorides; there are also smaller amounts of nitrates and comparatively slight amounts of bromides, iodides and fluorides. Metals are extracted from their ores chiefly by reduction with some form of carbon. In case of the oxides, this reduction takes place directly, according to this reaction: $2 \text{CuO} + \text{C} = 2 \text{Cu} + \text{CO}_2$.

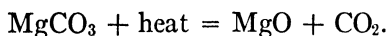
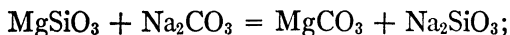
In case the metallic combination is a sulphide, the ore is first "roasted" in the air, whereby the sulphur is burned off and an oxide, which may then be reduced as above, is formed:



The native carbonates are reduced to oxides by calcination, as



The silicates must first be changed to carbonates by fusion with alkali carbonates; then the reduction may be carried on as before:



The types of furnaces in which above reductions are brought

about may, in general, be described as of three sorts — First, the blast furnace, in which the ore is mixed more or less intimately with the reducing substance in presence of a flux designed to combine with the impurities as fusible slag. Heat is applied from beneath the mixture. The reduction of iron ore furnishes an example of this type.

The second sort of furnace is illustrated by the reverberatory furnace, used in the separation of lead from the native sulphides. In this the flame is directed over the surface of the ore, the sulphur being removed as gaseous sulphur dioxide.

The third sort is the electric furnace of Moissan, made of lime or other infusible material, with large carbon electrodes. This furnace is used for the preparation of such metals as aluminium, sodium, potassium etc., by electrolysis of the fused chloride.

PROPERTIES OF THE METALS.

The following list shows the relative malleability of the metals, gold being the most malleable and nickel the least: Au, Ag, Al, Cu, Sn, Pt, Pb, Cd, Zn, Fe, Ni.

The relative toughness, or tenacity, of metals is shown by their order in the following list: Fe, Cu, Pt, Ag, Au, Al, Zn, Pb.

The ductility of metals ranges, from greatest to least, as follows: Au, Ag, Pt, Fe, Ni, Cu, Cd, Al, Zn, Sn, Pb.

Metals conduct heat and electricity in the same order, until tin is reached. From tin the order given is correct for heat but not for electricity: Ag, Cu, Au, Al, Zn, Cd, Sn, Fe, Pb, Pt, Bi.

The melting-point of the various metals is of considerable importance in the preparation of alloys. The following table has been compiled from the latest available results. The degrees given are according to the Centigrade scale:

Ir.....	2200°	Al.....	657°
Pt.....	1780°	Mg.....	500° (burns)
Ni.....	1450°	Sb.....	632°
Cast steel.....	1300°	Zn.....	418° (burns)
Cast iron.....	1200°	Pb.....	327°
Cu.....	1084°	Cd.....	322°
Au.....	1075°	Bi.....	268°
Ag.....	962°	Sn.....	232°

If lead, which is the softest of the common metals, is taken as a standard and considered as one, the other common metals are harder in the proportion shown in the following table, taken from Hall's "Dental Chemistry."

Pb.....	1.0	Sb.....	1.8
Sn.....	1.2	Zn.....	1.9
Cd.....	1.4	Pt.....	2.0
Al.....	1.5	Cu.....	2.4
Bi.....	1.6	Fe.....	2.4
Au.....	1.7	Ni.....	2.5
Ag.....	1.8		

The expansion of the various metals under the influence of heat is fairly constant, and *coefficients of expansion* have been determined. These represent the amount of linear expansion of the metals due to a rise in temperature of 1°C ., usually from 0° to 1° . The coefficients are not *absolutely* constant, and the amount of expansion observed between 0° and 1° may differ somewhat from that between 50° and 51° . The coefficients vary widely for the different metals; for instance, in passing from 0° to 100° , mercury expands $1/16$ of its linear measure, copper $1/598$, and platinum $1/1123$.

Hall's "Dental Chemistry" gives the following table of expansion from cadmium to platinum ($0^{\circ} - 100^{\circ}$):

Cd.....	$1/326$	Ag.....	$1/518$	Ni.....	$1/787$
Pb.....	$1/342$	Cu.....	$1/598$	Fe (cast).....	$1/934$
Zn.....	$1/343$	Bi.....	$1/617$	Sb.....	$1/952$
Al.....	$1/432$	Au.....	$1/689$	Pt.....	$1/1123$
Sn.....	$1/448$				

According to the kinetic-molecular theory, every metal has a certain tendency to pass into solution when immersed in a fluid. If the fluid contains the ions of some other metal of less relative electromotive force, the ions in solution will deposit upon the metal, while the metal-ion passes into solution; i.e., the one metal is precipitated by the other. In the list Au, Pt, Ag, Hg, Bi, Cu (Pb, Sn), Co, Cd, each metal precipitates all preceding it (lead and tin are too nearly alike for either to completely precipitate the other) and is precipitated by all which follow. All in the list are precipitated by Zn, Mg, Al, K, and Na.

Iron precipitates copper and the preceding metals, but it is only partly precipitated by those which follow.

The metals are electropositive in the following order, from zinc, the most positive, to gold, the least: Zn, Cd, Fe, Ni, Sn, Pb, Cu, Bi, Sb, Hg, Ag, Pt, Au; and carbon is negative to all. It will be noticed that this list of metals is the same, but in reversed order, and is arranged for the same reason as the list given in the paragraph above.

Thus if a battery is constructed with zinc, as represented in the cut (Fig. 6), and iron in place of the carbon, then the iron will be electronegative to the zinc, and hydrogen will be evolved from its surface; if, on the other hand, iron is used in place of the zinc, and the carbon remains as in the cut, the iron will be electropositive to the carbon, and oxygen will be evolved from its surface. This property of metals has a direct bearing upon dental science, because human saliva may be an exciting fluid for the generation of galvanic currents, its activity being increased by an abnormal reaction, either acid or strongly alkaline, and it is only necessary to place in the mouth properly related metals, as amalgam fillings or otherwise, to produce the elements of a galvanic battery.

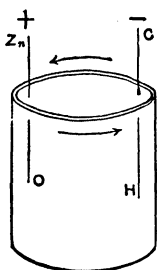


FIG. 6.

The currents thus generated are, of course, infinitesimal, but they are constant and may aid in the disintegration of fillings and in the solution of the constituent metals. Regarding the extent to which electric currents may exist in the mouth, see Miller's "Micro-organisms of the Human Mouth."

SILVER, AG (Argentum).

The Metal. — Atomic weight 107.88. Silver occurs free, in masses usually containing gold and copper; as sulphides, such as silver glance (Ag_2S) and in combination with sulphides of antimony, lead, and copper. It also occurs as silver chloride, (AgCl) known as "horn silver" or kerargyrite.

Properties. — Silver fuses at 954° C., forming a revolving globule on charcoal or plaster without oxidation.

At high temperatures, however, silver occludes or absorbs oxygen to the extent of twenty-two times its volume; but as the mass cools the absorbed gas is entirely given off, sometimes resulting in a roughened surface of the metal.

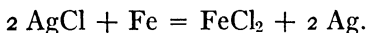
This property may be overcome by alloying with copper or by covering with a considerable layer of common salt.

Silver blackens in the presence of sulphur or hydrogen sulphide. The so-called oxidized silver is a result of heating the metal with a solution of potassium sulphide.

Silver dissolves in hot H_2SO_4 with evolution of SO_2 . It is readily soluble in nitric acid with formation of AgNO_3 , colorless crystals, without water of crystallization.

Silver amalgamates readily, and the "amalgamation process" is one of the important methods for its reduction from the ore.

This process, briefly, is as follows: The ore is roasted with salt, producing chloride of silver; this, in suspension in water, is reduced by metallic iron,



The mixture, treated with mercury, forms an amalgam from which the mercury can be driven off by heat.

Alloys. — Important alloys of silver are United States coin silver, consisting of silver 90 parts, copper 10 parts; and Sterling silver consisting of silver 92.5 parts, copper 7.5 parts.

Amalgam alloys contain from 50 to 60 per cent of silver, alloyed with tin and slight amounts of other metals such as copper, zinc, and gold. (See page 123.)

A silver platinum alloy used for base plates, clasps, etc., contains from 12 to 35 per cent platinum and is much harder than pure silver.

Von Eckart's alloy,* a French preparation, used for a similar purpose, contains 3.53 parts silver, 2.40 parts platinum, and 11.71 parts copper. Silver solders are alloys of varying propor-

* Hepburn, Notes on Dental Metallurgy, page 60.

tions of silver, copper, and zinc, the silver running from 60 to 80 per cent.

MERCURY, Hg (Hydrargyrum).

The Metal. — Atomic weight 200.6. Occurs as red sulphide, cinnabar, and in small quantities amalgamated with silver or gold or combined with chlorine or iodine. It is the only metal which is liquid at ordinary temperatures, solidifying at -39°C .

The molecule of mercury consists of a single atom.

Properties. — It boils at 360°C ., and this wide range of temperature throughout which the fluid form is maintained, together with its comparatively great coefficient of expansion (about $1/160$), makes it particularly suitable for use in thermometers and other instruments for measuring temperature or pressure.

At about 270°C . mercury combines with oxygen, forming the red mercuric oxide. At the boiling point, it readily leaves other metals, with which it has combined, making the purification by dry distillation a comparatively simple process. The redistilled and chemically pure mercury is usually obtained by distillation in *vacuo*.

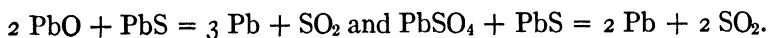
Certain mixtures of metals and mercury act as true chemical compounds, forming an exception to the foregoing statement regarding the separation of mercury by heat. (See page 116.)

Alloys. — Alloys of mercury are *amalgams* and will be considered as such.

LEAD, Pb (Plumbum).

The Metal. — Atomic weight 207.1. Occurs as sulphide (Galena), PbS ; in lesser quantities as native carbonate (Cerusite); also as phosphate, chromate, and sulphate.

Lead is reduced from the sulphide in a reverberatory furnace by a few simple reactions as follows: $3\text{PbS} + 5\text{O}_2 = 2\text{PbO} + \text{PbSO}_4 + 2\text{SO}_2$; then, by increasing the heat without access of air, the sulphur is driven off and the lead separates by two double decompositions,



Properties. — Melting-point from 325° to 335° C. Lead is one of the softest of the metals and can be easily cut with a good knife. It is a very poor conductor of electricity.

Presence of small quantities of antimony or arsenic tend to harden the metal.*

Lead is very easily separated from its compounds by reduction with carbon.

Lead is soluble in nitric or acetic acid, forming $\text{Pb}(\text{NO}_3)_2$ or $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.

Lead is also dissolved to a very slight extent by pure water containing oxygen, or by water containing CO_2 , mineral salts, or organic matter. It tarnishes in the air, with formation of a suboxide, Pb_2O .

Alloys. — Lead forms a large number of important alloys, among which are solders and fusible metals as given in Chapter V, and type metal which is an alloy of lead and antimony.

COPPER, Cu (Cuprum).

The Metal. — Atomic weight 63.57. Occurs free in vicinity of Lake Superior; also in western United States, Chili, and Spain, as sulphides, copper pyrites, chalcopyrite, CuFeS_2 ; and copper glance, chalcocite, Cu_2S . Malachite green and malachite blue are native basic carbonates of copper.

Properties. — Melting point 1084° C. Copper dissolves easily in nitric acid and with difficulty in hydrochloric acid; heated with sulphuric acid it forms copper sulphate, with the evolution of sulphur dioxide. Copper is second to silver as a conductor of heat and electricity. It expands slightly on solidifying and is corroded by carbon dioxide and moisture forming a green carbonate.

Alloys. — The alloy with mercury, amalgam, was formerly used in dentistry to a considerable extent (page 120). Copper alloys in all proportions with gold, silver, nickel, and zinc. It hardens silver and gold, and is used in the manufacture of coins, jewelry and the solders used in crown and bridge work. Copper

* Hepburn, Notes on Dental Metallurgy, page 137.

is also used in the preparation of bronze, brass, bell metal, dental gold, German silver, Mannheim gold, Mosaic gold, Dutch metal, and Aich's metal. For composition of copper alloys, see page 112.

BISMUTH, Bi.

The Metal. — Atomic weight 208. Bismuth does not occur in large quantities, but is usually found in the free state. Small amounts are obtained from the oxide, Bi_2O_3 , bismuth ochre, and from the sulphide, Bi_2S_3 .

It is easily identified by means of the blowpipe test on plaster with S and KI (page 89).

Properties. — Melting-point 268°C . It is a crystalline metal, expands upon cooling and readily unites with oxygen, burning with a bluish flame to bismuth oxide. At ordinary temperatures it is brittle and readily dissolved by nitric acid.

Alloys. — The most important alloys, from a dental standpoint, are the fusible metals, Melotte's metal, Wood's metal, Rose's metal, Newton's alloy, etc. (page 127).

Fletcher states that an amalgam with one part bismuth, fifteen parts tin, and fifteen parts silver, filed and amalgamated with four parts of mercury to one part of the alloy, will adhere to a flat dry surface and may be used as a metallic cement upon apparatus, giving an air-tight joint of great strength.

CADMIUM, Cd.

The Metal. — Atomic weight 112.4. Occurs associated with zinc in zinc blende. It is more easily volatilized than zinc, and advantage is taken of this fact in effecting its separation from that metal.

Properties. — Melting-point 322°C . Cadmium is a comparatively soft metal, though harder than zinc or tin. It is usually found in trade in the form of rods which crackle somewhat like tin when bent.

It dissolves slowly in sulphuric acid or hydrochloric acid with the evolution of hydrogen, and easily in nitric acid with the production of nitrogen oxides. It is also soluble in solution of

ammonium nitrate, forming cadmium nitrate and ammonium nitrite.

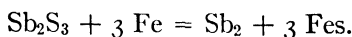
Alloys. — Cadmium is used as a constituent of fusible metals and rarely, in small proportion, in dental alloys. Its use in the latter case is objectionable on account of the production of yellow stain of cadmium sulphide which penetrates the dentine (page 121).

ARSENIC, As.

The Element. — Atomic weight 75.0. Arsenic is on the borderline between the metallic and non-metallic elements, its acid-forming properties predominating. It occurs associated with copper and iron sulphides, as arsenical pyrites, FeAs.FeS_2 ; as native sulphides, orpiment, As_2S_3 , and realgar, As_2S_2 ; also to some extent as the trioxide, As_2O_3 .

ANTIMONY, Sb (Stibium).

The Metal. — Atomic weight 120.2. Occurs native in Australia, and as the sulphide Sb_2S_3 , known as stibnite or antimonite from which it may be easily reduced by heating with metallic iron according to the following reaction:



Properties. — Brittle crystalline substance, volatile at high heat. It ultimately burns to antimonious oxide (Sb_2O_3). Soluble with difficulty in sulphuric or hydrochloric acids.

With nitric acid, antimony acts in a similar manner to tin, forming an oxide which may be antimonious (Sb_2O_3) or antimonie (Sb_2O_5) according to quantity and concentration of acid used (Prescott and Johnson's "Qualitative Chemical Analysis.")

Alloys. — Antimony is used in making type metal, Britannia metal, and rarely in low-grade dental alloys.

TIN, Sn (Stannum).

The Metal. — Atomic weight 119. Cassiterite, or tin-stone, nearly pure stannic oxide (SnO_2), is by far the most important source. The free metal has been found associated with gold.

Banca tin from the East Indies and block tin from England are pure varieties of the commercial article.

Properties. — Pure tin will give a peculiar crackling sound when bent, due to the crystalline structure of the metal. Tin is very malleable at the ordinary temperature, being fifth in the list of malleable metals (see page 94), but becomes brittle when heated to about 200° C.

Hydrochloric acid dissolves tin slowly, forming stannous or stannic chlorides according to the proportion and temperature of the acid used.

Cold dilute nitric acid will dissolve tin, forming stannous nitrate.

Metallic tin is not dissolved by strong nitric acid, but is converted into a white, insoluble metastannic acid. Hot dilute nitric acid will produce this same result. This acid, upon standing, changes to normal stannic acid, which is easily soluble in acids; hence, in making use of this reaction in the analysis of amalgam alloys, it is not well to allow the nitric acid solution of the alloy to stand too long before filtering.

Alloys. — Pewter usually contains Sn, Pb, Cu, and Sb, sometimes Zn; Rees's alloy contains Sn 20 parts, gold 1 part, and silver 2 parts. Tin is also a constituent of solders, fusible metals, Babbitt's metal, bell metal, and bronze.

An alloy of tin and mercury (tin amalgam) is used for "silvering mirrors."

GOLD, Au (Aurum).

The Metal. — Atomic weight 197.2. It is usually found uncombined, but mixed with various impurities. It occurs frequently as native alloys; of these, two might be mentioned: calverite, AuTe_2 , contains 40 per cent gold, and sylvanite, or graphitic tellurium, $(\text{AuAg})\text{Te}_2$, contains 24–26 per cent gold.

Gold is extracted from its ores in various ways, the simplest of which is that known as placer mining. This consists of a process of washing out the particles of gold, which separate themselves easily because they are heavier than the gravel and stones among which they are found. Hydraulic mining, the utilization of a great force of water to break up the auriferous

rock, has come to the aid of placer mining in getting the largest masses ready for the washing process. Other methods are quartz mining, in which mercury is used to attract the gold, and the chlorination process.

Properties. — Melting-point 1064° C. Pure gold is a soft metal of yellow color, unless in a very fine state of subdivision produced by the precipitation of the metal, when the color varies from purple to brown or nearly black. Gold is more malleable and more ductile than either silver or copper. Gold is second to silver as a conductor of electricity.

Gold is insoluble in simple acids, but may be dissolved in nitrohydrochloric acid (aqua regia) with formation of auric chloride. Gold also unites easily with bromine or iodine, forming AuBr_3 or AuI_3 .

Gold possesses the property of adhesiveness in a peculiar and very marked degree. By virtue of this the metal can be welded without heat; continued hammering tends to lessen or weaken this property.

When gold foil is heated to redness (annealed) it recovers the cohesive property which has been largely lost by hammering. The toughness and ductility are also increased. It is recommended that the heating be done in an electric furnace or on plates of mica or platinum, thus insuring uniformity of effect throughout the mass, which it is practically impossible to obtain by holding the metal in the flame. See *Dental Cosmos*, Vol. XLVII, page 233.

Non-cohesive gold, or gold in which the cohesive property cannot be developed by heating, may be prepared by alloying or treatment with carbon. **Corrugated gold** is of this variety, and is prepared, according to Essig, by carbonization of unsized paper in intimate contact with the metal. See Essig's "Dental Metallurgy," page 173, or Hodgen and Millberry's "Practical Dental Metallurgy," page 209.

Alloys. — Gold is alloyed with copper to make it harder and more durable for use in the manufacture of jewelry, plate, and coin. It is alloyed with silver for the purpose of reducing its melting-point. Copper and zinc, or copper, silver, and zinc

may be used in this way. (See page 131 for formulæ for gold alloys.)

The term "carat,"* as applied to gold, signifies $\frac{1}{24}$ part and is used as a measure of purity of an alloy, 22 carat gold being $\frac{22}{24}$ pure gold. Twenty carat gold is $\frac{20}{24}$ pure, etc. The amount of gold in a given alloy may be determined approximately by means of a device shown in Fig. 7, much used by jewelers, consisting of a series of standard alloys and a piece of stone upon which the test is made. The tips are standard alloys. Parallel markings are made on the stone with the alloy in question and with the tip supposed to correspond to it; then the addition of a drop of strong nitric acid to the marks and a careful comparison of their appearance will show if the two are of the same composition.

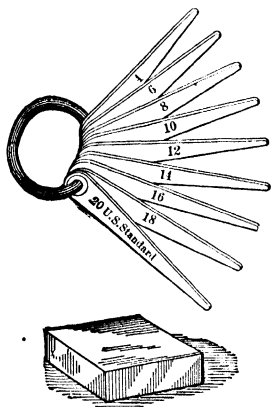


FIG. 7.

If the composition of an alloy is known, the value in carats may be determined by the following:

Rule to determine the carat of a given alloy: Multiply 24 by the weight of gold used and divide result by total weight

of alloy. For instance, if an alloy is made containing 9 parts of gold and 3 of another metal, the total weight will be 12 and the calculations $24 \times 9 \div 12 = 18$. The alloy is an 18-carat gold.

Gold may be *raised* to a higher carat by the following rule: Multiply weight of alloy used by difference between *its* carat and that of the metal to be added. Then divide product by the difference between the carat of the metal added and that of the required alloy. The figure thus obtained represents the total weight of *required* alloy. Subtract from this the weight of material taken and the difference is weight of pure or alloyed gold to be added. (From Hall's "Dental Chemistry.")

To *reduce* gold to a required carat, Essig takes the following

* The term carat is also used by jewelers as a unit of weight. The legal standard for U. S., since July 1, 1913, has been 200 milligrams.

rule from Richardson's "Mechanical Dentistry": "Multiply the weight of gold used by 24 and divide the product by the required carat. The quotient is the weight of the mass when reduced, from which subtract the weight of the gold used, and the remainder is the weight of the alloy to be added."

PLATINUM, Pt.

The Metal. — Atomic weight 195.2. Platinum, like gold, is found principally in the free or metallic state, often associated with the rarer metals such as iridium, rhodium, osmium, and palladium; also combined with gold, silver, and copper. A native arsenide, PtAs_2 , is found in the mineral sperrylite.

Properties. — Melting-point nearly 2000°C . Platinum solubilities are similar to gold; aqua regia forms the chloride PtCl_4 , or the chloroplatinic acid H_2PtCl_6 . Platinum is a white metal unaffected by oxygen or the fluids of the mouth, hence adapted for use in permanent dental appliances. When melted it absorbs oxygen in a manner similar to silver, and when finely divided (platinum black) will absorb or occlude gases to a remarkable degree, one part of platinum black, under favorable conditions, absorbing in this way over eight hundred times its volume of oxygen. As this occlusion necessarily means condensation of the gas, advantage may be taken of this property to bring about chemical union of gases which will not unite at ordinary temperatures, such as hydrogen and oxygen, oxygen and sulphur dioxide. Platinum black may be made by strong ignition of platinum chloride.

Alloys. — Platinum alloys quite easily with other metals, particularly lead; and platinum utensils may be destroyed by heating in contact with the compounds of metals easily reduced. Sulphur and phosphorus also attack platinum.

Platinum 90 per cent and iridium 10 per cent give an alloy harder, more brittle, and more resistant to chemical action than pure platinum.

An alloy of platinum and osmium is practically insoluble in acids, is very hard and capable of great expansion. Of the varying proportions of the two metals which may be used those of

1 to 10 per cent of osmium with 90 to 99 per cent of platinum prove the most successful. One part of osmium in such an alloy will take the place of two and one-half times its weight of iridium.

Note. — Iridium is a rare metal of particular interest in connection with the platinum alloy given above. Its symbol is Ir; atomic weight is 193.1; melting-point is about 2500° C. It occurs with platinum; also associated with osmium, with which it forms a very hard alloy insoluble in aqua regia.

“Platinum color,” for coloring enamel, is made, according to Mitchell’s “Dental Chemistry,” by precipitating platinum from a solution of PtCl_4 by boiling with KOH and grape sugar; then, grinding this finely divided platinum with feldspar in the proportion of one part platinum to sixteen parts feldspar.

PLATINUM METALS.

Under this head we may consider two groups, each consisting of three comparatively rare metals found associated with platinum and gold in platinum ores. In order of atomic weights, these metals are:

Ruthenium, Ru wt. 101	Osmium, Os wt. 191
Rhodium, Rh wt. 103	Iridium, Ir wt. 193
Palladium, Pd wt. 106.5	Platinum, Pt wt. 195 (194.8)

Native mixtures of these metals may contain 50–80 per cent platinum, iridium in moderate amount, and less than 2 per cent of any one of the others.

Ruthenium is slightly soluble in aqua regia, forming RuCl_3 .

Rhodium is insoluble in aqua-regia. Free chlorine on the metal forms RhCl_3 , insoluble.

Palladium is soluble in nitric acid and in aqua regia. The metal is remarkable for the amount of hydrogen which it is capable of absorbing, this being three hundred to one thousand times its own volume under varying circumstances.

Osmium, by action of strong oxidizing agents, chlorine or nitric acid, is converted into OsO_4 . This tetroxide is commonly known as osmic acid and is easily reduced to a finely divided,

black metallic deposit by organic tissue and particularly by fat; hence its use as a stain in histological work.

Iridium and **platinum** have already been considered.

IRON, Fe (Ferrum).

The Metal. — Atomic weight 55.84. Melting-point 1275° . Iron is widely distributed in nature, combined with oxygen as magnetite or magnetic iron ore, Fe_3O_4 ; as red hematite, Fe_2O_3 ; or brown hematite or limonite, $2 \text{ Fe}_2\text{O}_3 \cdot 3 \text{ H}_2\text{O}$; with sulphur as iron pyrites or fool's gold, FeS_2 ; and with carbon as spathic iron ore or siderite, FeCO_3 .

The reduction of iron from its ores is typical of one of the four general methods, that is, reduction by carbon. This is carried out in the blast or smelting furnaces, which are so constructed that a supply of coal, iron ore, and suitable flux may be introduced at the top of the furnace. The fusible slag consisting of the flux which has dissolved the impurities of the ore and the purified molten metal is drawn off from the bottom, thus admitting a continuous process. This melted iron, cast in molds as it comes from the furnace, constitutes our cast or pig iron, is brittle, and contains a considerable proportion of carbon, sometimes as much as 2.3 per cent, and other impurities.

Wrought iron is produced by working melted iron in specially constructed furnaces so that the greater part of the impurities are removed. It contains less than .6 per cent of carbon.

Steel may be made by a more perfect removal of impurities in the Bessemer converter and subsequent mixture of exact proportions of carbon, phosphorus, and manganese. Steel contains from .6 to 1.6 per cent of carbon.

Reduced iron, or "iron by hydrogen," is prepared by the reduction of the heated oxide or hydroxide in a stream of hydrogen gas, and consists of a very fine powder of pure metallic iron.

ALUMINIUM, Al.

The Metal. — Atomic weight 27.1. Aluminium, as a constituent of clay, feldspar, mica, etc., constitutes a considerable part of the earth's crust. The principal sources are cryolite, bauxite, and corundum.

Properties. — Melting-point 657° C. Aluminium is a silver-white metal, a good conductor of heat and electricity, and one of the lightest metals, its specific gravity being 2.58. Aluminium is reduced in an electric furnace by the aid of charcoal and copper with which it amalgamates (Cowle's process).

Alloys. — Aluminium alloys are not difficult to produce. The pure metal is used in making plates. A high proportion of aluminium in alloys is not desirable as it renders the alloy extremely brittle. Alloys containing from 5 to 30 per cent are of increasing importance. Aluminium bronze, consisting of copper with 5 to 12 per cent of aluminium, is used as a base for artificial dentures. An alloy used in the preparation of analytical balances and scientific apparatus, known as magnalium, contains aluminium and magnesium.

CHROMIUM, Cr.

The Metal. — Atomic weight 52. Melting-point 1510° C. Occurs as chrome iron ore or chromite, FeOCr_2O_3 .

Properties. — Chromium is a hard, grayish metal, not used as such in dentistry.

Alloys. — The important alloys of chromium are those in which it is combined with steel. Less than 1 per cent of chromium increases the strength, hardness and elasticity of steel to a marked degree. For this purpose, however, it is seldom used alone, usually being combined with nickel and sometimes with vanadium. Chromium alloys with difficulty with copper, but with cobalt it will mix in all proportions. Silver and cadmium do not dissolve chromium.

COBALT, Co.

The Metal. — Atomic weight 58.97. Cobalt occurs in nature as an arsenide CoAs_2 , smaltite; also CoAsS , cobaltite. These ores are poisonous and have, in times past, caused the miners so much trouble that the name cobalt was applied to them, the word meaning, "A demon or mountain sprite." Metallic arsenic has also been called cobalt. These facts are probably responsible

for an undeserved reputation which is sometimes attached to the pure oxide of cobalt.

NICKEL, Ni.

The Metal. — Atomic weight 58.68. Melting-point 1450° C. It occurs associated with cobalt, sometimes with iron or with copper as a sulphide. Also it is found combined with magnesium as a double silicate called garnierite, $\text{NiMg}(\text{SiO}_3)_2 \cdot 3\text{H}_2\text{O}$. Natural alloys of nickel with arsenic and with antimony are to be included among the sources of the metal.

Properties. — The metal is white and hard, and has a high melting-point. It is soluble in dilute mineral acids, most easily in nitric. It is the least malleable of the common metals. It tarnishes very slowly in the air.

Alloys. — The principal alloys are German silver, containing copper, nickel, and zinc, and an alloy of 25 per cent nickel and 75 per cent copper, used by the United States Government in making five cent pieces.

In contact with saliva, German silver changes rapidly, and in consequence is usually gold plated when used for orthodontia appliances.

Nickel plating. — Nickel is largely used for plating steel and copper. In this process, metallic nickel is made the positive pole and substances to be plated are attached to the negative pole of a battery giving not more than five volts. The electrolyte is a solution of nickel and ammonium sulphate made slightly alkaline with ammonia water. Nickel deposits on copper in a much more satisfactory manner than on iron, and from warm solution better than from cold.

The following formulæ are also recommended by Prinz:*

Nickel sulphate.....	10 parts
Sodium citrate.....	9 “
Distilled water.....	280 “
Nickel and ammonium sulphate.....	70 parts
Boric acid.....	25 “
Distilled water.....	1000 “

In any case, use pure nickel in sheet form as an anode.

* Dental Formulary.

MANGANESE, Mn.

The Metal. — Atomic weight 54.93. Occurs chiefly as the dioxide MnO_2 , pyrolusite.

Manganese dioxide may be reduced by carbon at very high temperatures (above 1100°C.) and is usually prepared by reduction with aluminium or with carbon in an electric furnace. Manganese is a soft metal and fairly permanent in the air if free from carbon, but the more carbon it contains, the more rapidly it will oxidize. Manganese forms a definite carbide, Mn_3C , which reacts with water in the following manner.



ZINC, Zn.

The Metal. — Atomic weight 65.37. Occurs chiefly as the carbonate, ZnCO_3 , calamine. A native carbonate of zinc is also known as smithsonite. The sulphide ZnS (zinc blende), and the silicate are also natural sources of the metal.

Note. — The name calamine has also been given by Professor Dana of Yale to a silicate of zinc, $\text{H}_2\text{Zn}_2\text{SiO}_5$.

These ores of zinc, whether sulphide or carbonate, upon roasting in air, are converted into oxide, and the oxide is easily reduced by carbon to metallic zinc.

Properties. — Melting-point 420°C. (burns). The metal is bluish-white in color, is brittle at ordinary temperatures, but malleable and ductile at 140° to 150°C. At 200°C. , however, it again becomes brittle and fuses as above stated at 420°C. At 950° , zinc boils and may be distilled; in air it ultimately burns to a white oxide. Whenever zinc ores are sufficiently rich in the metal, the pure zinc may be separated by heating with carbon out of contact with the air to a temperature considerably in excess of its boiling-point; the zinc then distils and may be condensed.

Alloy. — Zinc is of considerable importance from a dental standpoint, the metal itself being used in the manufacture of counter-dies and solders; and, according to Mitchell's "Dental

Chemistry," it may be advantageously used in the proportion of 1 to 1.5 per cent in silver-tin amalgam alloys. "It tends to control shrinkage, imparts a 'buttery' plasticity to the amalgam, adds to the whiteness of the filling and assists in the maintaining of its color." See also page 122.

Of the metals of Groups V and VI, Magnesium alone is of importance as a metal.

MAGNESIUM, Mg.

The Metal. — Atomic weight 24.32. Principal sources are the carbonate, MgCO_3 , magnesite, and a double carbonate, $\text{CaMg}(\text{CO}_3)_2$, dolomite. The sulphate MgSO_4 occurs in the mineral kieserite in the "Stassfurt deposit." "French chalk" (or talcum), soapstone, and meerschäum consist of magnesium silicate in varying states of purity.

Asbestos is a double silicate of magnesium and calcium.

Properties. — Magnesium is a silver-white metal occurring in trade as ribbon or powder. It burns easily in air, forming MgO and traces of Mg_3N_2 and producing a white light which is used in photography. It is a light metal, having a specific gravity of 1.75.

Alloys. — For the alloy with aluminium, see page 108. The amalgam alloys are not practical, as they heat and swell in a manner which renders them practically useless.

CHAPTER V.

ALLOYS, AMALGAMS, CEMENTS.

An intimate union of two or more metals, usually produced by fusion, forms an **alloy**. Such a union of one or more metals with mercury is an **amalgam**.

An alloy designed to be used in the preparation of dental amalgams is known as an **amalgam alloy**.

Some metals can be fused together in all proportions, as lead and silver. Others can be made to unite only in limited proportions, as lead and zinc. Lead will carry only 1.6 per cent of zinc, while zinc will unite with only 1.2 per cent of lead. Excess in either case separates out.

The **properties** of an alloy are, as a rule, the modified properties of its constituent metals. An exception to this rule is found in the sonorous quality of bell-metal and like alloys, this being hardly a property of the constituent metals at all.

Following are some of the more common alloys. The proportions given are general formulæ and may, as a rule, be varied considerably:

Aich's metal,* Cu 60 per cent, Zn 38.2 per cent, Fe 1.8 per cent.

Aluminium bronze, yellow, resembles gold, Cu 92, Al 8.

Bell-metal, Cu 80, Sn 20.

Brass, Zn 1 part, Cu 2 parts.

Britannia metal, Cu 2, Sn 82, Sb 16.

Bronze, Cu 65 to 84, Zn from 31.5 to 11, Sn from 2.5 to 4.

Coin silver, Ag 90, Cu 10.

Dental alloys, see page 123.

Dental gold, Cu 85, Zn 15.

Dutch metal, Cu 84.5 per cent, Zn 15.5 per cent.

* Hepburn.

German silver,* Cu 50, Ni 30, Zn 20.

Gun metal, Sn 11, Cu 100.

Mannheim gold, Cu 75 per cent, Zn 25 per cent.

Mosaic gold, Cu 50 per cent, Zn 50 per cent.

Solder, see page 129.

Sterling silver must contain 92.5 per cent Ag.

Type metal, Pb 78, Sb 15, Bi 7.

For fusible metals (Mellot's, Wood's, Rose's, etc.), see page 127.

All alloys (excluding amalgams) are solid at ordinary temperatures with one exception; this one is an alloy of one part potassium with three parts sodium.

The **melting-point** of an alloy is often lower than that of the metals entering into its composition and usually lower than the mean melting-point of its constituents.

In **making alloys** the tendency to separation of the several metals is greater if the alloy is allowed to cool slowly; hence three essentials in the process are: **complete fusion**, which makes possible **thorough mixing**, and after this has been attained **rapid cooling**. As the fused mass is to be cooled as quickly as possible after fusion is complete, it is desirable to use the least amount of heat that will effect the desired result. To this end, fuse first the metal with the lowest melting-point, then add other metals in the order of their melting-points. The more difficultly fusible metal will, in a sense, dissolve in the more easily fusible metal; an alloy is formed and its temperature has been kept far below the melting-point of the high fusing constituent. This general rule, however, may be modified by the proportion of metal used; thus, in making a silver-tin amalgam-alloy containing 60 per cent of silver, it is better first to melt the silver under a flux of carbonate of sodium or borax to prevent superficial oxidation, then add the tin, and lastly any other metal to be used. The **mixing** is attained by stirring with a **wooden stick** and the **cooling** by turning quickly into a cold clean mold. For class work or in making small amounts (20 grams) of alloy,

* Composition of different samples of German silver may differ widely; some contain about 2.5 per cent of iron and the amount of copper may vary from 40 to 60 per cent.

the Fletcher melting arrangement shown in Fig. 8 is very convenient. The metals are melted in the graphite crucible; then the whole contrivance is tipped up and the melted metals flow back into the ingot mold. If the alloy is to be used in the preparation of dental amalgams it must be reduced to fine turnings or filings suitable for ready amalgamation. This is best accomplished in the laboratory by means of a coarse file, the ingot being held by a vise. The fine particles of iron must next be carefully removed with a magnet, and then the filings may be annealed if desired.

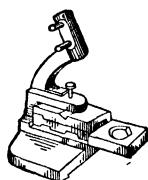


FIG. 8.

The **annealing** of the amalgam-alloys may be accomplished by placing the freshly cut sample in a dry test-tube and keeping the test-tube in boiling water for ten or twelve minutes. It has been claimed that this process is one of superficial oxidation, and the changes produced seem to be consistent with this theory. Again, it is claimed that the change is a molecular one of some sort, due to change of temperature, and Professor G. V. Black has shown that an alloy will anneal as rapidly in an atmosphere of nitrogen as of oxygen. The modification of properties produced by annealing varies somewhat with the composition of the alloy; for instance, the liability to discoloration is less in the annealed than in the unannealed sample, if the alloy contains silver and tin, or silver, tin, and zinc, but if copper is a constituent the reverse condition has been found to exist.

It has been shown that the freshly cut amalgam alloys require more mercury for amalgamation than the annealed alloy. The annealed alloy also is slower in setting and contains a smaller proportion of impurities (metallic oxides) which detract from the strength of the amalgam.

Professor Black has shown that while it may be possible to stop the process of annealing at such a point that a given alloy will neither shrink nor expand, it is easy to carry the process too far, and the farther it is allowed to go the greater the shrinkage. It is probably true that the exact effect of annealing will vary with the composition of the alloy, and with different proportions of metals in alloys of the same general composition.

In annealing *platinum* a high degree of heat is required, but the heat should be raised gradually, and in this case, as with gold, the electric furnace furnishes an ideal method.

Eutectic Alloys. — The term eutectic signifies lowest melting-point or freezing-point, and is perhaps best illustrated by water and salt.

If a salt solution, so made that it contains 23.6 per cent by weight of sodium chloride, is cooled to a temperature of -22°C. , the two substances crystallize together in the form of a very intimate mechanical mixture of ice and salt crystals. This is known as a eutectic mixture, and these proportions are the eutectic ratio for salt and water.

A decrease in the temperature of a solution which contains less than 23.6 per cent of salt causes the excess of water to crystallize in a comparatively pure form, leaving a brine of constantly increasing degree of concentration until the eutectic proportions are reached. If the salt solution were stronger than 23.6 per cent, the salt would crystallize out, leaving a brine of decreasing concentration. Both of these latter crystallizations, however, would take place above -22°C. ; the point where the eutectic mixture crystallizes, therefore, is the lowest possible for a mixture of this particular nature.

In exactly this way, a eutectic alloy is one which has the lowest possible melting-point obtainable by use of the given constituents; and in similar manner also, when an excess of one or the other metals is used, we may regard the mixture as a solution of the eutectic alloy in an excess of metal.

The physical differences between the eutectic alloy and "the solid solution" may be shown by microscopical examination, the eutectic mixture being much more intimate in character than the other. This examination is made by reflected light upon a surface polished as perfectly as possible. The method of procedure is as follows: a thin piece of alloy is polished by the use of emery disks and paper of varying grades until the surface is as smooth as possible, then the polishing is completed by the use of the very finest paper, then by a rapidly rotating wheel covered with cloth upon which jeweler's rouge has been rubbed.

The most satisfactory results are obtained if the surface of the alloy is kept wet.

The specimen may be mounted in soft wax contained in a brass ring with perfectly parallel edges, as it is essential that the polished surface be parallel to the microscope stage. After the examination of the polished surface it may be etched by various chemicals, such as nitric and hydrochloric acid, and again examined.

As an illustration of what may be accomplished in this way, the following cuts are inserted. These are taken from "Physical Chemistry of the Metals" by Schenck and Dean, and reproduced here with their permission.

AMALGAMS.

In general, amalgams may be made in three different ways: first, by direct union of the constituents, as in the manufacture of sodium amalgam (page 119); second, by electrolysis of strong solutions of metallic salts in presence of mercury, as in copper amalgam (page 120), and third, by double decomposition, as illustrated in the preparation of ammonium amalgam (page 119).

The nature of the amalgam seems to vary with the composition; that is, some amalgams are apparently true chemical compounds, others are solutions of one metal in another, or in mercury, while still others are mixtures of these two, or solutions of the compound; for example silver, gold, and copper will form definite compounds with mercury from which the mercury cannot be separated by heat even at a temperature of 450° C. — nearly a hundred degrees in excess of the boiling-point of mercury — but these compounds readily unite with larger proportions of mercury in the formation of amalgams. Also platinum, tin, cadmium, and bismuth do not retain mercury at 450° C.; and potassium and sodium form definite crystalline compounds with mercury.

Amalgams possess the peculiar property of "setting," or hardening, within a short time after mixing. This in some cases



FIG. 9. — Zn-Cd Alloy, Eutectic with Embedded Cadmium Crystals.

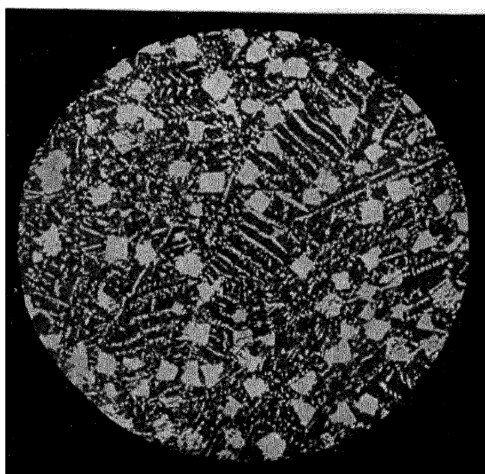


FIG. 10. — Bearing Metal Alloy of Tin, Antimony and Lead.

seems to be a process of crystallization, and in all cases is probably due to molecular rearrangement of some sort.

After an amalgam has "set" to a sufficient extent to make it hard to work, it may be softened by application of gentle heat. Continued reheating is detrimental to the quality of the amalgam, and should be avoided; this is particularly true of copper amalgam. Sometimes it is also possible to restore the

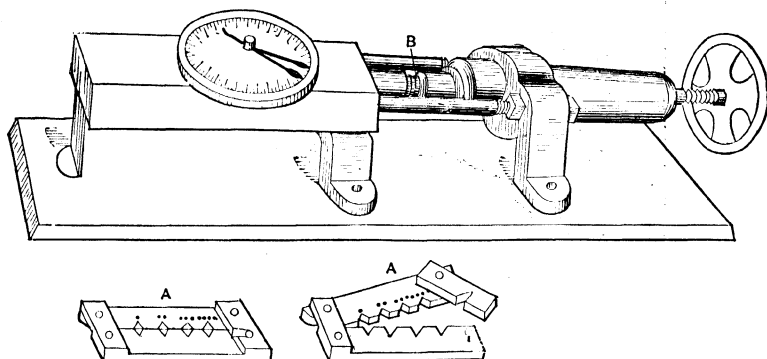


FIG. 11.

plastic quality of an amalgam by adding a further slight amount of mercury, but the union of the second lot of mercury after the first has partly hardened is very unsatisfactory and results in a weakened product.

Flow of Amalgams.—This property may be defined as the tendency to flatten or change shape under stress or pressure. It is common to most amalgams (copper amalgam being an exception, according to Dr. Black), and is possessed by many alloys other than amalgams.

Tests for "flow," and much better for "crushing strength," may be made with the "dynamometer" on cubes of alloy or amalgam measuring $1/10$ inch each way, and the results expressed in percentage of increase or decrease of one dimension. The dynamometer used for this purpose is pictured in Fig. 11 and is a modification of the apparatus devised by Dr. Black and described on pages 408 and 409 of the *Dental Cosmos*, Vol. 37, A-A being the molds in which the

cubes of amalgams are set and *B* the point in the apparatus where the cube, after setting, is introduced with a pair of fine forceps. The dial is supplied with two hands, one of which flies back the instant the cube breaks, the other remaining to indicate the number of pounds applied necessary to crush the cube. The cubes of $1/10$ inch are best suited for students' practice, with a dial constructed to record 250 pounds pressure. For accurate comparisons of thoroughly made amalgams, the cubes must be made smaller.

Binary amalgams, as they are sometimes called, are those consisting of only one metal besides mercury. These are rarely used in dental practice, but from them the properties of the amalgamated metal are most easily observed.

Sodium amalgam may be made by direct union of the constituent elements. The mercury should be placed in an open dish under a hood, and the sodium added in *small* well-cleaned pieces.

The union is accompanied by a slight hissing noise, an elevation of temperature and evolution of vapor carrying more or less mercury, hence dangerous to breathe. An amalgam containing 1 per cent sodium is a viscid liquid; if it contains 5 per cent sodium it is a hard solid, and intermediate percentages give varying degrees of firmness. Sodium amalgam, if made with arsenic-free mercury, is a very convenient reagent to use in making Fleitmann's Test (page 33).

Aluminium amalgam is easily made with aluminium filings and mercury or dilute solution of mercuric chloride. This amalgam decomposes water at ordinary temperatures, giving free hydrogen and aluminium hydroxide.

Ammonium amalgam has no use in dentistry, but it is of interest in that it represents the nearest approach to the isolation of the purely hypothetical metal, ammonium. It is easily made by adding sodium amalgam to a *cold* saturated solution of ammonium chloride, thus illustrating the third general method of preparation of amalgams. It rapidly decomposes at ordinary temperature with the liberation of free hydrogen, ammonia-gas and metallic mercury. The hydrogen thus

liberated exhibits the properties of nascent hydrogen, indicating that in the amalgam it existed in true chemical combination, that is, NH_4 , rather than in any physical solution. At ordinary temperature ammonium amalgam is a soft, pasty, very porous mass, but at much reduced temperature it becomes solid and crystalline, although at -39° (the freezing-point of mercury) hydrogen and NH_3 are still given off.

Copper Amalgam is by far the most valuable of this class of amalgams. It may be made by amalgamating precipitated copper after moistening it with nitrate of mercury (Essig). The precipitated copper may be prepared by action of metallic zinc in a slightly acid copper sulphate solution, but must be thoroughly washed with hot water to free it from zinc chloride. The amalgamation may be effected by use of mortar and pestle. Rollins' method* by electrolysis of strong copper sulphate solution is rather unwieldy, but illustrates very well the second general process for the manufacture of amalgams.

Copper amalgam, according to Black, is absolutely rigid after it has once set and does not flow even to a slight extent. It is fine-grained and very hard. It is reduced in strength by reheating and does not expand or contract. In the mouth, copper amalgam dissolves with comparative rapidity owing to the ready formation first of copper sulphide, then, by the oxidation of this compound, of the sulphate. It blackens rapidly and in consequence of the tendency just mentioned, to dissolve, it may penetrate the dentine and thus discolor the tooth itself.

Gold amalgam is readily made, but does not, by itself, harden well. An amalgam containing one part of gold to six of mercury will crystallize in four-sided prisms (Litch).

Magnesium amalgam may be easily produced, but, like the amalgams with aluminium or sodium, it decomposes water with the evolution of hydrogen.

Platinum amalgam is very smooth, is formed with difficulty unless the platinum is *very* finely divided, and, like gold, does not harden well.

* Details of this method may be found in the *Boston Medical and Surgical Journal*, February, 1886; also in Mitchell's 'Dental Chemistry.'

Silver amalgam is easily made but tends to expand.

Tin amalgam, alone, shrinks badly.

Zinc amalgam, readily made, is white, but too *brittle* to be of service.

Cadmium amalgam may be easily made at ordinary temperature, "sets quickly, and resists sufficiently, but fillings containing it gradually soften and disintegrate and may stain the dentine bright yellow by formation of cadmium sulphide." (Mitchell.)

EFFECT OF VARIOUS METALS IN AMALGAM ALLOYS.

With the properties of these simpler combinations before us, it becomes easy to understand the effect the addition of the various metals will have upon the properties of a silver-tin alloy; for practically *all* amalgam alloys are silver-tin alloys, either simple or combined with one or more other metals.

Silver and tin are the most valuable constituents of amalgam alloys. Silver is essential to the proper setting and hardening of the amalgam. It tends to increase expansion and to hasten setting, while tin possesses the opposite characteristics. Combined with tin in the proportion of 65 per cent silver to 35 per cent tin, it forms an amalgam alloy perhaps more largely used than any other. It was this combination that Dr. Black succeeded in "annealing to zero," that is, so that upon testing it showed neither expansion nor contraction.

Pure silver-tin alloys will flow from 2.5 to 10 per cent.

Dr. C. M. McCauley, in an article on amalgams published in the *Dental Cosmos* for February, 1912, states that the formula of 65 per cent silver and 35 per cent tin will produce an amalgam which gives no shrinkage if the freshly cut alloy is used, but that upon annealing the alloy it was necessary to use about 74 per cent silver. He further states that 5 per cent of copper for an equivalent of silver increases the strength of amalgams made from silver-tin alloys.

Dr. McCauley also tells us that a contraction of one ten-thousandth of an inch will admit organisms producing caries into a tooth cavity, but that an expansion of the finished filling

of about one twenty-thousandth of an inch is a desirable result.

The larger the proportion of tin the easier will the alloy cut, but the coarser will be the filings.

Zinc added to a silver-tin alloy tends to whiten the amalgam, hastens setting, increases the flow, and, according to Essig, "causes a great but slow expansion."

Dr. McCauley, quoted above, states that zinc is unfavorable in its action on other metals in a dental alloy and detrimental when used to the extent of only 1 per cent, because of its tendency to produce a constant expansion for several months, even though tests made during the first few days were satisfactory.

Cadmium, see page 121.

Antimony gives a fine-grained alloy, and when the silver is less than 50 per cent is supposed to control shrinkage.

Bismuth will increase the flow of the amalgam; it is sometimes used in low-grade silver-tin alloys to control shrinkage.

Copper tends to diminish flow and gives a strength under pressure, sets quickly, gives better margins, and by some is believed to have preservative influence on the tooth substance, but the more copper in an alloy the more rapidly does it discolor.

Gold. — From 3 to 7 per cent of gold in a silver-tin alloy diminishes shrinkage, helps the color and adds to crushing strength. The filing from such an alloy will be very fine.

Dr. Black says 5 per cent of gold gives a softer working property but retards setting of the amalgam, and makes it otherwise difficult to give a good finish to the filling (*Dental Cosmos*, Vol. 38, page 988).

Platinum, according to Black, is not a desirable addition to a silver-tin alloy. It gives an alloy furnishing *very* fine filing, which produces a dirty working, slow-setting amalgam.

Excess of Mercury. — In the preparation of an amalgam from a dental alloy it is usual to add more mercury than the finished product requires and then squeeze out the excess between the fingers or otherwise. In filling a cavity, still more mercury is forced out, so that the composition of the deeper portions of a filling varies from the outer portions and probably

accounts for the inequalities in expansion or contraction. The excess of mercury from the surface of a filling may be absorbed by a little hot gold or pure tin or by finely-divided silver.

Following is a short list of dental alloys, most of which may be easily prepared:

	Sn	Ag	Au	Cu	Zn	Sb
Arlington's (S. S. White's).....	57.5	42.5				
*(C. A. S.) alloy, C. Ash Sons Co.....	27.16	66.54		5.02	0.90	
Chase copper-amalgam alloy.....	50	50		10		5
Chase's incisor alloy.....	40	50				10
*Fellowship alloy.....	26.80	67.45		5.73	0.55	
Flagg's submarine alloy.....	35	60		5		
Fletcher's gold alloy (old).....	56	40	4			
High-grade alloy (7½% gold).....	41.5	49	7.5		2	
Harris's amalgam alloy.....	48.1	40		4.9	7	
King's occidental alloy.....	54.75	42.75			2.5	
*Odontographic alloy.....	26.48	66.87	0.28	6.21	trace	
*Standard alloy.....	35.03	53.55	8.82	2.76		
Standard dental alloy (Eckfeldt).....	40.6	52	4.4	3		
60% silver alloy.....	40	60				
Temporary alloy.....	88	10			2	
*True dentalloy.....	27.13	65.91		5.21	1.52	
*Twentieth century.....	27.13	67.03		4.87	1.10	

* Analyses by Dr. P. J. Burns of the Mass. Inst. Technology, reported in the *Journal of the Allied Societies*, June, 1908.

These formulæ have been selected from various sources with a view to giving the student opportunity to study effects obtained by varying percentages of tin and silver, and by introduction of other metals, copper, zinc, etc.

The excess of mercury which has to be squeezed out of an amalgam carries with it more or less of the constituent metals. Hall found that whatever the amount of mercury expressed, it carried just about 1 per cent of tin. In the author's experience, this amount has reached nearly 1½ per cent of tin. Silver is carried out to a much less extent than tin, so it is not impossible to make an amalgam carelessly and squeeze out enough mercury to change the proportion of silver and tin in the alloy. This change will, of course, be very slight, but we have seen that the contraction and expansion of amalgams may be affected by slight changes in composition.

TESTS FOR AMALGAMS.

From the work on testing amalgams two results are to be expected.

First, the student experiences the satisfaction of first-hand knowledge, and acquires the habit (to a certain extent) of asking questions which can be answered only by laboratory experiments. Second, he learns the effects of the addition of the various metals on amalgam alloys and, in a general way, the methods of testing.

Of course, it is recognized that the results obtained are not to be considered as valuable as those of the commercial laboratories, such as those described in the *Journal of the National Dental Association* for June, 1919, by A. W. Gray, Ph.D.

For accurate methods in this work, the student is referred to the article just mentioned, and, if the equipment described there is accessible, the author recommends these methods. However, the equipment described by Dr. Gray is not available to the average dental student; hence the author's introduction of apparatus and of tests which to some may seem out of date. With careful attention to detail and with uniform conditions, comparative results of surprising accuracy may often be obtained with apparatus which is more or less crude and inexpensive.

Color Test. — This is made upon a freshly amalgamated alloy, rolled into about the shape and size of a small pea, with a view to determining the amount of discoloration the amalgam is liable to undergo in the mouth.

A ball of amalgam, carefully smoothed on at least one side, is placed for forty-eight hours in a saturated solution of hydrogen sulphide, and after that time its color is compared with other amalgams similarly treated, or with amalgam of a similar composition which has not been treated.

Test for Expansion or Contraction. — Black has shown that tests of this nature, to be of any value, must be made in such a way that the *amount* of change in the volume can be measured, and that the simple method of packing glass tubes and using colored ink is wholly unreliable.

The author uses for this purpose an apparatus similar to one described by Vernon J. Hall. The amalgam is packed closely into a "well" in a steel block, then the block is placed in the apparatus so that a counterpoised steel plunger rests on the column of amalgam. This plunger is operated by a very long needle and attached at a point so near the pivotal support of the needle that a rise or fall of the plunger of $1/2500$ of an inch moves the tip of the needle, at the scale, $1/16$ of an inch,

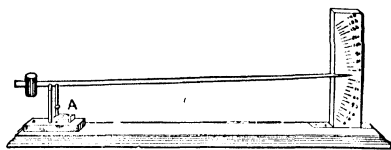


FIG. 12.

or one degree. If the needle rises half a degree, which may easily be read, it would indicate an expansion of the amalgam of $1/5000$ of an inch.

There are two wells in each block, both of exactly the same depth. The figure given above will make this explanation easily understood, *A* being the steel block carrying the amalgam.

Test for Crushing Strength and Flow. — The test is made with Dr. Black's dynamometer (page 118) upon cubical blocks of amalgam which have been allowed to "set" for at least two days, and which measure $1/10$ of an inch each way.

Specific gravity may be obtained by weighing the sample first in water, then in air, and dividing the weight in air by the difference between the two weights obtained.

It is instructive to make these tests on amalgam from alloys of varying composition, also on annealed and unannealed alloys of the same composition.

Test for Hardness. — The hardness of an amalgam is shown, in a way, by the result of the crushing-strength test; but here, without the best of testing machines, the personal factor is apt to be so great as to make the test of little value — perhaps of the least value of any test applied to amalgams. The hardness test can be made directly on the alloy, and, even with the simple

instrument herein described, will give much more accurate results than are usually obtained by student work upon amalgams. In studying the effect of variations in the composition of alloys, the hardness test is instructive; e.g., copper will give

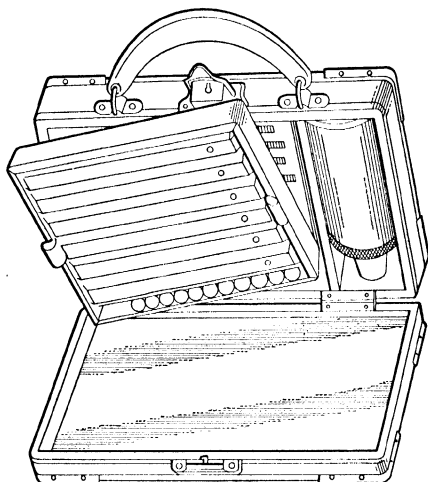


FIG. 13. — Hardness Tester.

edge strength and increase hardness of certain amalgam combinations, but its addition to a silver-tin alloy does not harden the alloy in the way we were led to expect by early writers on the subject.

Hardness may be determined by any of the machines on the market devised for the purpose. Above is a cut of one such machine, reproduced from Eimer and Amend's catalog.

The test is made by driving a hardened metallic ball, always with uniform force, into or against, the smooth surface of the alloy.

Satisfactory results may be obtained by the use of the ordinary "prick punch" with a spherical cap over the point of the punch. In this case the diameter of the resulting "dent" should be measured microscopically by means of a micrometer eye-piece.

The impression shown in Fig. 14 was obtained from a high-grade dental alloy containing both copper and zinc. A differ-

ence 0. 2 or 3 per cent of copper will show a difference in the diameter of the impression of $\frac{1}{2}$ to $1\frac{1}{2}$ microns.

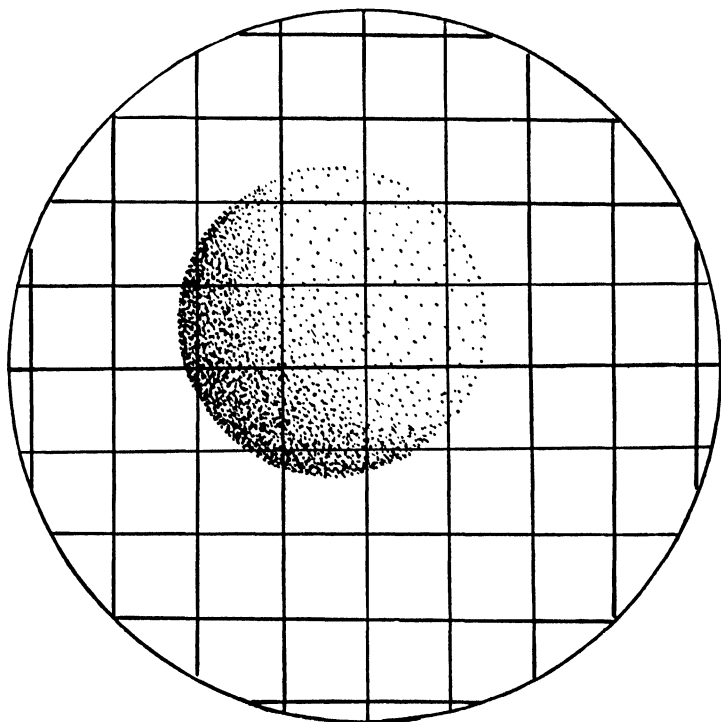


FIG. 14.

FUSIBLE METALS.

Under the head of fusible alloys, properly come many of the alloys considered on page 129 as solders. The fusible alloy usually contains lead or bismuth, together with tin and occasionally cadmium. This may be mixed in such proportions that the melting-point may be anything desired, down to 63° C. These alloys are largely used in the dental laboratory. Mellot's metal, composed of bismuth eight parts, tin five parts, and lead three parts, is perhaps the most serviceable. This melts at about the temperature of boiling water. Wood's metal, melting at

about 65°C ., is composed of bismuth four parts, tin one, lead two and cadmium one. Rose's metal is bismuth two parts, tin one, and lead one. This melts at about 95°C .

Babbitt Metal, much used in the manufacture of dies, is composed of copper one part, antimony two, and tin eight. The formula of common Babbitt metal on the market will be found to differ somewhat from the above and is not so well suited for dental purposes.

According to Essig's "Dental Metallurgy," Dr. C. M. Richmond used a fusible alloy in crown and bridge work, which he states is as hard as zinc and can be melted at 150°F . and poured into a plaster impression without generating steam. The formula of this alloy is as follows: Tin twenty parts, lead nineteen, cadmium thirteen, and bismuth forty-eight. The following fusible-metal alloys are also suitable for student practice.

Tin	Lead	Bismuth	Melting-point of Alloy.
1	2	2	236°F . or 113°C .
5	3	3	202°F . or 94°C .
3	5	8	197°F . or 92°C .

The fusing-point of an alloy may be determined by melting it under a liquid of sufficiently high boiling-point and then carefully noting the temperature at which the melted alloy solidifies.

Approximate results may be obtained by watching carefully the melting of a very thin strip of alloy.

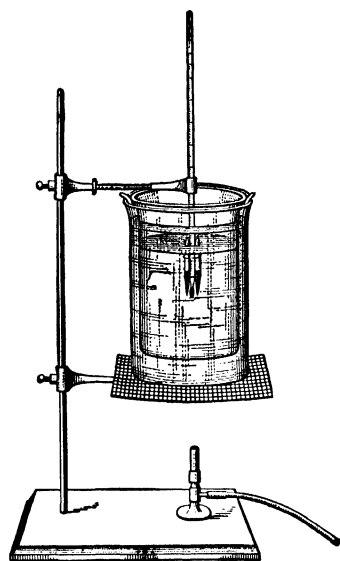


FIG. 15. — Apparatus for Taking Melting-Point.

Care must be taken that the temperature of the alloy is exactly the same as recorded by the thermometer. To insure this in the case of an alloy with low melting-point, it is usually sufficient to place the alloy in water or brine in a test-tube which is immersed in a beaker of similar fluid; then, by raising the heat gradually with con-

stant stirring and by taking the mean of two or three determinations, fairly accurate results are obtained.

SOLDERS.

Solders are alloys used in joining pieces of metal of the same or of different kinds. One of the constituent metals of the alloy forming the solder is usually the same as the surface upon which it is to be used; hence the various metals require solders of special composition; for instance, common solder is entirely unsuited for soldering aluminium or gold.

Common Solder is composed of tin and lead in different proportions. The larger the proportion of tin the finer is the solder, and the following three grades may usually be obtained: "fine" or "hard" (tin two parts and lead one), "common" or "medium" (tin and lead equal parts), "coarse" or "soft" (tin one part and lead two parts).

In soldering metals, it is absolutely essential that the surfaces be kept clean and free from the superficial coating of oxides which may form easily with the elevated temperature employed in the process. Soldering acid and the various fluxes serve this purpose. Soldering acid is an acid solution of zinc chloride usually made by taking a few ounces of strong hydrochloric acid and adding zinc as long as the metal dissolves. Among the substances which may be used as a flux to prevent oxidation, rosin and borax are the most common.

Soft Solders are those fusing below a red heat, and include the common solders above mentioned, also the most fusible solders containing bismuth. These last are more properly fusible metals and are discussed under that head.

Solders for Aluminium. — Aluminium solders with considerable difficulty, owing in part to the low melting-point of the metal, also to the fact that aluminium is attacked by alkalies, including borax, which makes it necessary to find some substitute for this convenient flux. Essig recommends a flux consisting of three parts of copaiba balsam, one part of Venetian turpentine, and a few drops of lemon-juice. The mixture is to be used in the same manner as soldering acid with a solder con-

sisting of zinc from eighty to ninety-two parts, aluminium from eight to twenty parts. Fused and finely powdered silver chloride may also be used as a flux, the salt being reduced and the silver forming a superficial alloy. Richards recommends a solder for aluminium consisting of tin twenty-nine parts, zinc eleven parts, aluminium one part, phosphor-tin one part.

Hall says that a solder which he has found very satisfactory may be prepared from aluminium forty-five parts, tin forty-five, mercury ten; further, that the following formulæ suggested by Schlosser are particularly adapted to soldering dental work, since they resist the reaction of corrosive substances.

Platinum-Aluminium Solder.		Gold-Aluminium Solder.	
Gold.....	3. parts	Gold.....	5 parts
Platinum.....	0.1 part	Copper.....	1 part
Silver.....	2 parts	Silver.....	1 "
Aluminium.....	10 "	Aluminium.....	2 parts

For soldering articles of aluminium, the following solder is given in the *Pharmaceutical Era*, January 10, 1895: Silver two, nickel five, aluminium nine, tin thirty-four, and zinc fifty parts, to be used without flux. See also *Dental Cosmos* for 1906 (page 115).

Solder for Brass requires a high heat for fusion, and on this account is known as hard solder.

Edwinson gives the following formulæ: (1) copper thirteen parts, silver eleven; (2) copper one part, brass one, silver nineteen; (3) brass five parts, zinc five, silver five. The flux for brass soldering is powdered borax, which may be mixed with water to a paste and applied with a feather or a small brush.

Solder for Gold.—Gold soldering is the most particular work of this class which the dentist has to do. There are a few requirements for a good gold solder which may be noted and which are also applicable to the other solders mentioned: (1) The color should be as nearly as possible that of the metals upon which it is to be used. (2) The solder should have a fusing-point but very slightly below that of the metal to be soldered. (3) The solder should flow freely.

Litch gives the following instructions for making a zinc-gold solder which will have the above-mentioned properties:

"To make the zinc-gold solder take one pennyweight of the same gold upon which it is to be used and add one and a half grains of zinc. If this is done in a crucible in the furnace, first fuse the gold (which should either be clean scraps or be cut from the plate; never use filings for this purpose), using but little borax; when thoroughly fused take the crucible in the tongs, drop the zinc into it, give the crucible a rather vigorous yet skilful shake to assist in mixing its contents, but without causing any to be thrown out, and immediately pour into the previously prepared ingot mold. This must be done very quickly or the solder will require too high a heat for the fusion on account of a large proportion of the zinc being volatilized or oxidized and thus be lost as alloys."

Essig gives the following formulæ for alloys of gold employed in dentistry as solders:

NO. 1. 14 CARATS FINE.

American gold coin.....	\$10.00
Pure silver.....	4 dwts.
Pure copper.....	2 "

NO. 2. 14 CARATS FINE.

American gold coin.....	16 dwts.
Pure copper.....	3 dwts. 18 grs.
Pure silver.....	5 "

NO. 3. 14 CARATS FINE.

Pure silver.....	2½ dwts.
Pure copper.....	20 grs.
Pure zinc.....	35 "
18-carat gold plate (formula	

No. 11)..... 20 dwts.

NO. 4. 15 CARATS FINE.

Gold coin.....	6 dwts.
Pure silver.....	30 grs.
Pure copper.....	20 "
Brass.....	10 "

NO. 5. 16 CARATS FINE.

Pure gold.....	11 dwts.
Pure silver.....	3 " 6 grs.
Pure copper.....	2 " 6 grs.

NO. 6. 16 CARATS FINE.

Pure gold.....	11 dwts. 12 grs.
Pure copper.....	1 dwt. 12 "
Pure silver.....	3 dwts.
Pure zinc.....	12 grs.

NO. 7. 18 CARATS FINE.

Gold coin.....	30 parts
Pure silver.....	4 "
Pure copper.....	1 part
Brass.....	1 "

No. 8. 20 CARATS FINE, FOR CROWN AND BRIDGE WORK.

American gold coin (21.6 carats fine) \$10 piece	258	grs.
Spelter solder	20.64	"

No. 9. 20 CARATS FINE, SAME USE AS No. 8.

Pure gold	5	dwt.
Pure copper	6	grs.
Pure silver	12	"
Spelter solder	6	"

No. 10. 20 CARATS FINE, FOR CROWN AND BRIDGE WORK.

Zinc	1½	grs.
Pure gold	20	"
Silver solder	3	"

No. 11. DR. C. M. RICHMOND'S SOLDER FOR BRIDGE WORK.

Gold coin	5	dwt.
Fine brass wire	1	dwt.

No. 12. DR. LOW'S FORMULA FOR SOLDER FOR CROWN AND BRIDGE WORK, 19 CARATS FINE.

Coin gold	1	dwt.
Copper	2	grs.
Silver	4	"

Solder for Platinum. — Platinum utensils may be soldered with any good gold solder, and a flux may be used if desired. When, however, the solder is used in connection with porcelain work, it must be pure gold or a gold and platinum alloy. A 25 per cent platinum alloy has been found to give excellent results. The following in regard to gold and platinum alloy is from the *Dental Review*, August, 1905:

"The colleges and text-books tell us the proper proportions of gold and platinum alloys, but they usually fail to tell us *how to do it*. In most cases the platinum appears in white spots on the plate without producing a proper alloy. Take a small piece of 22-carat gold and fuse it under the blowpipe. Then work in all the platinum you can in small pieces until it has taken up all that is required. It will produce a small button of a white alloy which is very brittle. Add this alloy in required proportions to the gold in the crucible and it will produce a real platinum alloy. By this method you can make clasp gold that

is pretty nearly as stiff as a steel spring and yet will roll and work without fracture." (Mark G. McElhinney, Ottawa, Canada.)

Solder for Silver. — Solder for silver usually consists of alloys of silver and copper with sometimes zinc and sometimes tin. Litch recommends a silver solder made by alloying pure silver with one-third its weight of brass. Brann't's "Metallic Alloys" gives alloys of silver and copper only. Hall recommends silver eight parts, copper one, and zinc two. In the preparation of solder containing copper, zinc, or tin, the use of a flux is necessary to prevent the formation of metallic oxide. For this purpose borax is usually employed. The silver, constituting, as it does, the greater proportion of the alloy, should be melted first and be covered with considerable borax. When this has been thoroughly fused, the other metals may be added and mixed by agitation or by stirring with wood. Finally, the solder may be cast in the usual ingot mold.

DENTAL CEMENTS.

Dental cements may be classified as ordinary oxyphosphates of zinc cements, copper cements and synthetic cements which include the artificial enamels. These three kinds will include by far the larger proportion of cements in common use, and all contain more or less oxyphosphate of zinc.

Oxyphosphate of Zinc. — The oxyphosphate cement is usually made by adding a powder, consisting largely of pure oxide of zinc, colored by a slight amount of other metallic oxides, to a liquid consisting of deliquesced phosphoric acid (or a solution of phosphoric acid in which zinc phosphate, and possibly slight amounts of other phosphates, have been dissolved), till a putty-like mass results, which rapidly hardens and becomes capable of receiving a considerable polish. When the phosphoric acid used is the glacial acid, the cement may be spoken of as a metaphosphate, because the glacial acid, before the addition of water, and to a certain extent afterwards, is actually metaphosphoric acid, HPO_3 . The metaphosphoric acid, by boiling with water or gradually by addition of water without boiling, becomes the orthophosphoric acid (H_3PO_4).

Hall's "Dental Chemistry" takes the following tests from Flagg's "Plastics and Plastic Filling," as characterizing a good oxyphosphate cement.

General Tests. 1. When first mixed it should yield a tough mass which, when removed from the spatula, does not adhere to the fingers and can be rolled into a pliable pellet.

2. It should have a glassy surface; and, at the end of two or three minutes, it should rebound when dropped upon wood, glass, or porcelain.

3. At the end of five minutes it should be quite hard and should sound like porcelain when tapped.

4. After ten or fifteen minutes it should be dented with difficulty, and when broken should show a clean, sharp fracture.

5. After twenty minutes it should be very hard, and should be capable of taking a good burnish.

6. In thirty minutes it should have little or no acid taste.

Arsenic is a frequent impurity in both zinc oxide and phosphoric acid, and if present is very liable to produce an irritating cement, sometimes causing considerable trouble; hence, the material entering into the composition of any dental cement should be free from arsenic (see pages 32 to 36 for arsenic tests).

The purer the zinc oxide and the phosphoric acid from which the cement is made, the more durable it is found to be; so, aside from any question of irritation, it is quite necessary for the sake of the cement itself that the ingredients be pure.

It is not intended to give the impression that the liquid should consist *only* of glacial phosphoric acid or the powder *only* of oxide of zinc. A cement thus made would set so rapidly that it would be of no practical value. The resulting mass would also probably be crumbly. The powder or the liquid, one or the other, is usually mixed with phosphates of the heavy metals which would be insoluble in water, but which would dissolve in the strong phosphoric acid.

A pure zinc oxide may be made by calcining the precipitated carbonate of zinc, $\text{Zn}_6(\text{OH})_6(\text{CO}_3)_2 + \text{heat} = 5 \text{ ZnO} + 2 \text{ CO}_2 + 3 \text{ H}_2\text{O}$. The heat should be below 500° F.; if it is too high the color suffers, becoming yellowish.

Another method of making pure oxide of zinc is given as follows: Dissolve pure zinc in nitric acid, evaporate to dryness, and heat till fumes cease to be given off. The mechanical action of the escaping oxides of nitrogen is said to leave the zinc oxide in the form of a *very* fine powder.

A pure phosphoric acid can be made from the ortho-acid by heating till the white fumes begin to come off, then heating to redness, cooling and dissolving in water to a thick syrup. In mixing cements, the powder should be worked into the liquid till the desired consistency is obtained.

Oxyphosphate cement and all cements having zinc oxide for a base tend to dissolve in the fluids of the mouth, lactic acid and ammonium salts being particularly good solvents for this class of compounds. The addition of ferric oxide to oxyphosphate cement increases resistance to disintegration. One part of ferric oxide to six to ten of zinc oxide is recommended by Rollins in the *International Dental Journal*.

Oxychloride of Zinc is more easily soluble than oxyphosphate. It shrinks more, but is credited with a preservative action on dentine and hence is used to some extent as a lining.

The powder of the oxychloride cement is zinc oxide with sometimes a little borax, or silica, or both, added. A good oxychloride cement will set in fifteen or twenty minutes, but keeps on growing harder for several hours. The following formula is recommended.

Oxide of zinc 10 grams, borax 0.1 gram, and powdered silica, 0.2 gram.

Transfer to clay crucible and calcine for one-half hour in furnace at bright-red heat. Pulverize, sift, and bottle. The liquid to be used with this powder consists of 10 c.c. of pure hydrochloric acid *saturated* with pure zinc and filtered through glass wool.

Oxysulphate of Zinc. — This is used still less than the oxychloride. It is non-irritating, dissolves easily, and is comparatively soft. The following formula is taken from Hall's "Dental Chemistry."

Ten grams oxide of zinc, 4 grams sulphate of zinc. Dry, mix, calcine for one-half hour, and sift.

Liquid to be used with the powder may be made by dissolving 2 grams of zinc chloride in 10 c.c. of water. This gives a turbid solution and should be shaken when used.

Oxyphosphate of Copper cement (Ames's) consists of the usual powder and liquid. The powder contains oxides of copper, iron (slight amount), cobalt, and zinc, and, of course, is black in color. The liquid is phosphoric acid holding in solution a certain amount of phosphate of zinc.

The cement resulting from this combination was found to be hard, showing practically no change of volume and resisting the solvent action of the saliva.

White Copper cement. The powder of this preparation has been found to consist of 95 per cent oxide of zinc and 5 per cent of cuprous iodide.* The presence of iodine can be easily demonstrated by treatment with nitric acid and the solution of the iodine in chloroform.

Tin cement. Dr. Arthur Scheuer, of Teplitz, Bohemia, recommends a preparation composed of a finely pulverized tin sponge and zinc oxide mixed with glacial phosphoric acid. "The powder is of a light-gray color, becoming slightly darker when mixed with the acid, but regains its original color after setting. A tin-cement filling can be easily inserted and when polished it has a metallic appearance." (*Dental Cosmos*, May, 1904.)

Artificial Enamel. — Several preparations have been put on the market under this name, the manufacturers of each claiming that it makes a much harder cement and one which resists disintegration to a much greater extent than the ordinary zinc preparations.

The specifications of a German patent, under which one of these preparations is manufactured, claim that the powder consists of a mixture of the oxides of beryllium and silicon, together with alumina and lime. The liquid consists of a 50 per cent solution of orthophosphoric acid in which aluminium phosphate and zinc phosphate have been dissolved.

* W. V. B. Ames, D.D.S., *Dental Review*, June, 1914.

A qualitative analysis confirms the claim of the patent specifications both in regard to the composition of the liquid and the presence of oxide of beryllium in the powder, and it is probable that the value of these preparations depends largely upon the proportion of beryllium entering into their composition.

This statement from an earlier edition has been quoted * with the assertion that about one-quarter of the powder of Ascher's artificial enamel is beryllium oxide.

Beryllium is a rare metal which occurs naturally with aluminium as a silicate, also as beryllium silicate (beryl), colored forms of which are used as precious stones. Beryllium forms basic compounds of such a character as to make it suitable for use in dental cement.

The cement powders may be tested for beryllium as follows: Fuse a little of the powder with sodium carbonate (or the double sodium potassium carbonate); dissolve the fused mass in dilute hydrochloric acid; evaporate to dryness and heat to 120° C. to dehydrate the silica; take up in water with a little hydrochloric acid and filter; to the filtrate (probably containing Al, Be, Zn, and Ca) add a little ammonium chloride, and an excess of ammonium carbonate, $\text{Al}(\text{OH})_3$, $\text{Be}(\text{OH})_2$, and CaCO_3 , will be precipitated. The beryllium, however, is easily soluble in the excess of $(\text{NH}_4)_2\text{CO}_3$. Warm (not boil) and allow to stand for some time to insure complete separation of aluminium. Filter. Boil the filtrate for a long time; the beryl-

(*Note.* — $\text{Al}(\text{OH})_3$ is much less soluble in solution of $(\text{NH}_4)_2\text{CO}_3$ than in either NH_4OH or even NH_4OH and NH_4Cl .)

lium and some zinc will then be precipitated. Filter and dissolve precipitate off paper in dilute hydrochloric acid. To the filtrate containing BeCl_2 and ZnCl_2 add NH_4Cl in excess and NH_4OH , which will give a precipitate of $\text{Be}(\text{OH})_2$. If beryllium and zinc only are present, the separation by boiling may be unnecessary.

The liquid may be tested for dissolved phosphates by diluting with water and adding ammonia till alkaline; if the mixture remains clear, phosphates of alumina, calcium, or zinc are

* Dental Summary, 1915, p. 56.

absent. Care should be used, however, in the addition of the ammonia, as an excess of this reagent will redissolve phosphate of zinc.

If the ammonia is too strong, a precipitate of ammonium phosphate may be obtained, but this may be easily redissolved by the simple addition of water.

Silicate cements, synthetic cements, and synthetic porcelain are names applied to later preparations containing silica, aluminium, and sometimes magnesia in addition to usual cement constituents. Dr. Ames is authority for the statement that beryllium is useful chiefly for advertising purposes.

It might be well to remember in this connection that the natural sources (ores) of beryllium available in Europe are richer in beryllium than those obtained in this country.

Dr. E. O. Hile, in the *Dental Digest* for 1913, page 441, says that the production of de Trey's synthetic porcelain is based upon a study of the setting of Portland cement. The liquid of this porcelain contains a smaller proportion of acid than any other cement liquid.

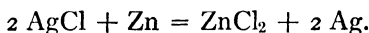
RECOVERY OF RESIDUE.

Gold. — The gold scrap may be recovered in two ways: first, by fusion with suitable flux; second, by dissolving in aqua regia and precipitation of the metal. In the first method it is necessary to remove the impurities by mechanical means as far as possible, then mix the fairly clean gold waste with potassium nitrate and a little borax, and fuse in a clay crucible. The gold will separate as a button at the bottom of the thoroughly fused slag.

In the second method the scrap gold is dissolved in aqua regia and the resulting solution of gold chloride is precipitated with ferrous sulphate or oxalic acid. The latter precipitant, although working more slowly than the iron, does not precipitate platinum, hence in case platinum is present it is the better reagent to use. The precipitated gold is next filtered, thoroughly washed, and fused in clay crucible under borax and potassium nitrate.

Silver. — The recovery of silver is best accomplished by dissolving the scrap or waste in nitric acid and precipitating as chloride, then reducing the chloride to metallic silver either by treatment with pure zinc or by fusion with sodium carbonate. If tin is present in the scrap, the nitric acid will form metastannic acid, a white insoluble powder rather difficult to filter. Hence, it is better to wash this by decantation several times with distilled water, which will remove practically all the silver. From the nitric acid solution the silver may be precipitated by salt or hydrochloric acid. This precipitate must be washed till the wash-water is practically free from chlorine, then dried and fused with sodium carbonate, whereupon a button of pure silver will be obtained.

If preferred, the precipitated chloride of silver may be washed once by decantation, then agitated with pure zinc, when the following reaction takes place:



The finely-divided silver (in the form of nearly black powder) must be washed free from chlorine, carefully dried and fused under carbonate of sodium; or, after drying, it may be weighed and dissolved at once if a solution is desired. If the silver residue contains mercury, this may be driven off by heat before solution is attempted.

Mercury. — Mercury which has been used in making amalgams is best purified by distillation. Mercury which needs simply to be freed from dirt, dust, or slight traces of other metals may be purified as follows: If a piece of filter-paper is fitted closely in a glass funnel, a pin-hole made in the joint and the paper thoroughly wetted with water and the mercury to be purified placed on the paper, the heavy metal will run through the pin-hole, leaving practically all the dirt clinging to the wet filter-paper. Such mercury may also be cleansed by filtering through chamois skin.

In case the mercury contains slight amounts of other metals, if it is digested with a very dilute nitric acid, the acid will generally first dissolve the impurities and afterwards a little of the

mercury itself. Then thorough washing with water will remove all excess of acid and all soluble salts which may have been formed. Pure mercury should have no coating of any sort on its surface, and if a few globules are allowed to run down a smooth inclined plane, they should leave no "tail" behind.

CHAPTER VI.

VOLUMETRIC ANALYSIS.

STANDARD SOLUTIONS.

Volumetric analysis is the determination of the quantity of a particular substance contained in a given sample by means of volumetric or standard solutions. By means of standard solutions, it is possible to determine easily and quickly the strength of a peroxide of hydrogen solution, the percentage of silver in an amalgam alloy, or the amount of gold in a plate or solder; and it is volumetric analysis, thus specialized and adapted to dental purposes, that we shall consider.

The standard solution may be so prepared that it has an arbitrary or special value, such, for instance, as the silver-nitrate solution sometimes used in determining the amount of chlorine in urine, 1 c.c. of this solution being equal to 10 milligrams of salt (NaCl); or its standardization may be made with reference to the molecular weights of the reagents employed, so that solutions of a similar nature will be of equivalent values.

Normal and decinormal solutions, or the volumetric solutions of the U. S. Pharmacopœia, are of this character.

A normal solution may be defined as one containing the hydrogen equivalent of the reagent in grams per liter. This definition may be explained by saying that the solution contains the molecular weight of the reagent in grams per liter provided the reagent is of univalent basicity; otherwise, such part of the molecular weight is taken as represents the molecule reduced to a univalent basicity.

For example, a normal (N/1) solution of hydrochloric acid or of potassium hydroxide would contain the molecular weight per liter; one of sulphuric acid or of calcium hydrate would contain one-half the molecular weight per liter.

If the process involves oxidation, the oxidizing power of the reagent relative to one atom of hydrogen determines the proportion of the molecular weight to use; for example: iodine (I_2) and hydrogen peroxide (H_2O_2) will each require half the molecular weight per liter to make a normal solution, because in each case the molecule will "oxidize" two atoms of hydrogen. So $K_2Mn_2O_8$, which will furnish five atoms of available oxygen capable of oxidizing ten atoms of hydrogen, requires only one-tenth of its molecular weight in 1000 c.c. to produce a normal solution.

It will be seen from the above explanation that equal volumes of normal solution will always bring about exact reactions.

The normal solution should not be confused with molar ($M/1$) solution used elsewhere in the book, which contains the molecular weight of the reagent in grams per liter without regard to the hydrogen equivalent; for example: a molar solution of H_2SO_4 contains 98 grams, while a normal solution contains 49 grams per liter.

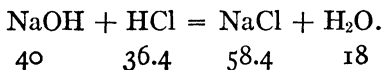
Exact reactions between molar solutions are produced when volumes corresponding to the respective number of molecules taking part in the reaction are used. See Exp. 25, page 170.

The *normal factor* is the weight of reagent contained in *one cubic centimeter* of the normal solution.

The volumetric process and the use of the normal factor will be most clearly understood by the explanation of a specific example.

Suppose that we have prepared a normal solution of NaOH and wish to ascertain the strength of a sample of dilute HCl. The normal solution will contain the molecular weight in grams of NaOH per liter or 40 grams absolute NaOH.

The molecular weight of HCl being 36.4 (36.37), a normal solution of HCl will contain 36.4 grams absolute HCl; and, if a liter of normal NaOH were added to a liter of normal HCl, *exact* neutralization would result:



The one liter of normal alkali (containing 40 grams NaOH) is exactly neutralized by 36.4 grams of HCl, or 1 c.c. of normal alkali by 0.0364 gram of HCl. 0.0364 is normal factor of HCl.

Now, if by our process of analysis we find that it takes just 21 c.c. of the NaOH solution to exactly neutralize 10 c.c. of HCl solution, 1 c.c. of NaOH being equal to 0.0364 gram HCl, 21 c.c. of NaOH will be equal to 0.0364×21 , or 0.7644 gram HCl, or 10 c.c. of the HCl solution contains 0.7644 gram of absolute HCl, equivalent, approximately, to 7.64 per cent.

It has become apparent that in carrying out this process three things are absolutely necessary:

1. Methods for the preparation of standard solutions.
2. Apparatus for *accurate* measurements of both the standard solution and the unknown.
3. Means for determining just when the point of exact neutralization is reached. This point is known as the **end point** and is shown by **indicators** of various kinds.

Preparation of Standard Solutions. — Experience has shown that normal solutions are in many cases less convenient to work with than those much more dilute, both on account of the keeping qualities of the standard solution and the accuracy of manipulation; and, for the purposes of dental chemistry, a *decinormal* or one-tenth normal solution represented by N/10 will generally be used.

In working with an N/10 solution, the factor used in calculations of results will be one-tenth of the normal factor and is termed an N/10 *factor*. Other fractional proportions of the normal solution may be used, as the centinormal, N/100, or seminormal, N/2. While the decinormal solution contains one-tenth of the hydrogen equivalent of reagent in grams per liter, and this amount is very easy to calculate, it is often very difficult to *weigh out* the exact amount required. For instance, we want an N/10 solution of HCl. HCl is a gas soluble in water and the strengths of the solutions vary greatly, so we cannot weigh out 3.637 grams of absolute HCl to put in 1000 c.c. of water, though we know this is just the amount necessary to produce our N/10 solution. Thus, one of the first practical

difficulties in making up standard solutions is to find some substance which can be weighed accurately and the exact chemical composition of which may be relied upon.

Crystallized oxalic acid is such a compound, although care must be taken that the crystals are dry and yet contain all their water of crystallization; in other words, are actually represented by the formula $\text{H}_2\text{C}_2\text{O}_4, 2 \text{H}_2\text{O}$. Fused carbonate of sodium is another such compound. If the purest obtainable bicarbonate of soda is fused till no further change takes place, cooled, and powdered, the product is pure enough for the preparation of a standard solution for ordinary use.

For the preparation of volumetric solutions it is necessary to have a balance which will weigh accurately to at least two decimal points. It will be much better to have a balance sensitive to one milligram. Balances of this sort, inclosed in a glass case, can be obtained at a very reasonable price. Figure 16 on page 145 represents such a balance.

It is also essential to have flasks capable of holding 100, 250, 500, and 1000 c.c., carefully graduated on the neck, represented in Fig. 17, page 145.

Graduated cylinders (Fig. 18) are not so well suited for the preparation of standard solutions, as the greater breadth of the column of liquid makes accurate reading much more difficult.

Small cylinders of 100 c.c. or less are useful in making up odd amounts of solution.

In the process of analysis it will be necessary to have pipettes (Fig. 19) measuring 5 and 10 c.c., also a burette (Fig. 20), from which the standard solution may be used. The burettes may be had in a variety of styles and sizes, a very serviceable one being of 25 c.c. capacity and graduated in tenths of a cubic centimeter. It may have a glass stop-cock or it may be furnished with a glass tip with rubber connector and pinch-cock.

A set of measuring-instruments which have been carefully compared with one another should be kept; that is, the 1000-c.c. flask should be exactly filled by taking the 100-c.c. flask full to the mark just ten times, thus enabling one accurately to take aliquot parts of any given solution.

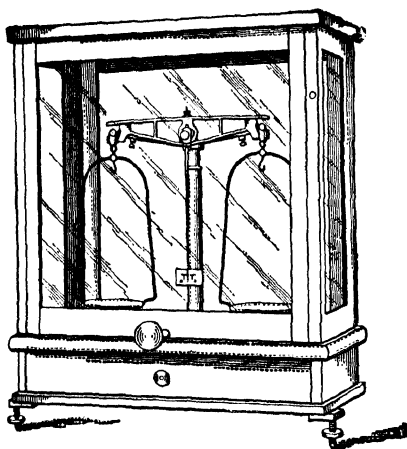


FIG. 16.

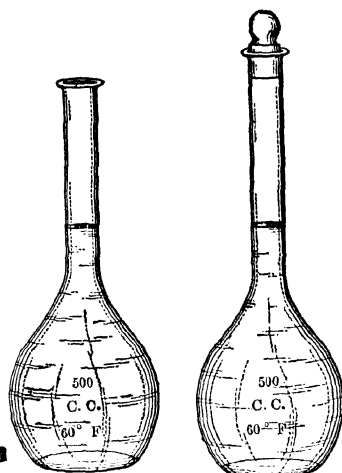


FIG. 17.

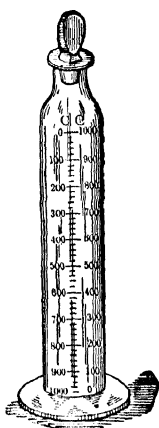


FIG. 18.

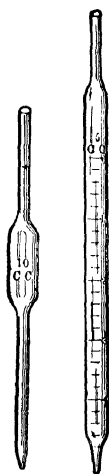


FIG. 19.

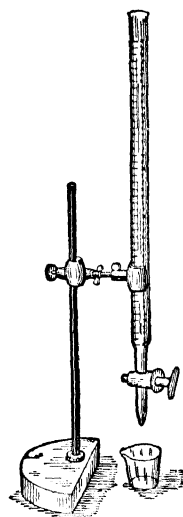


FIG. 20.

INDICATORS.

The third requisite for carrying out a volumetric process is a method for determining the end point of the reaction; that is, we must know when there has been a sufficient quantity of a standard solution added to an unknown solution. *Phenolphthalein* gives a red color with alkalis, which is discharged by the addition of acid till the solution becomes colorless as it becomes neutral or acid. *Litmus* gives a blue color with alkalis and a red with acids. *Methyl orange* can be used with carbonates and mineral acids; it does not work so well with organic acids. The color is pink in acid and yellow in alkaline solution. *Lacmoid* is useful in cases where the acid properties of such salts as alum or zinc chloride might interfere with the use of litmus or phenolphthalein. The different indicators do not all change color at exactly the same point in the process of neutralization, and it is possible for a solution to be alkaline to litmus and acid to phenolphthalein, at the same time. Hence uniformity in the use of indicators is desirable. In physiological chemistry, Congo red, tropæolin *oo*, and dimethylaminoazobenzene are also used.

The end point may be indicated by excess of a standard solution if it happens to be highly colored, as potassium permanganate. Thin starch paste is used as an indicator in operations involving the use or liberation of free iodine. Other indicators will be considered as we have occasion to use them in the various analytical processes.

The processes of volumetric analysis may be divided into three classes: first, *acidimetry* and *alkalimetry*; second, *oxidation* and *reduction*; third, *precipitation*.

ACIDIMETRY AND ALKALIMETRY.

Acidimetry and alkalimetry include the use of all standardized solutions, either acid or alkaline, in neutralizing solutions of unknown strength of an opposite character. For instance, the strength of vinegar is determined by neutralizing a known volume with standard alkali.

For present purposes two standard acids and one standard alkaline solution will be sufficient.

DECINORMAL OXALIC ACID.

The first of these may be decinormal oxalic solution prepared from recently recrystallized and carefully dried acid. The composition of these crystals should be $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$, having molecular weight of 126.

If we consider the reaction involved in the neutralization of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 + 2 \text{NaOH} = \text{Na}_2\text{C}_2\text{O}_4 + 2 \text{H}_2\text{O}$) we see that twice as much alkali is required as would be necessary to neutralize a monobasic acid like HCl. Hence, to obtain our hydrogen equivalent, we divide the molecular weight of oxalic acid by two, which will give us a weight in grams to be dissolved in sufficient water to make one liter of normal solution. A decinormal solution will be one-tenth of this strength.

For class use, each student may prepare 500 c.c. of this solution by dissolving 3.15 grams of pure crystallized oxalic acid in water and diluting to a half-liter. The graduated flasks are usually constructed to be used at a temperature of 60°F . or 15°C ., and for accurate work solutions must be brought to this temperature. After the oxalic acid solution has been prepared, the decinormal alkali may be made as follows:

DECINORMAL SODIUM HYDROXIDE.

Weigh out carefully $2\frac{1}{2}$ grams of caustic soda or 3 grams of caustic potash and dissolve in less than 500 c.c. of distilled water. After the solution has thoroughly cooled, fill a burette with it. Place 10 c.c. of standard acid, previously prepared, in a white porcelain dish of about 250 c.c. capacity, add 20 c.c. distilled water and 2 or 3 drops of phenolphthalein (2 per cent phenolphthalein in alcohol and water, equal parts); then carefully run in the alkali solution from the burette, with constant stirring, until a permanent pink tint is produced. This process is known as "titration," and will hereafter be so designated.

The work will be more satisfactory if the titration is made

for the appearance of color rather than the disappearance of color, as would have been the case had the standard acid run *into* the measured alkali solution.

The Calculation. — Supposing it has taken 8.2 c.c. of the alkali to exactly neutralize the 10 c.c. of $N/10$ acid; it follows that in the 8.2 c.c. there is sufficient alkali to equal or to make 10 c.c. of an $N/10$ alkali solution; hence we may add 1.8 c.c. of distilled water to every 8.2 c.c. of alkali solution, thereby reducing it to decinormal strength. Practically, we should take 410 c.c. of alkali solution and in a graduated flask make it up to 500 c.c. with distilled water. It will be necessary to make several titrations and average the results before making the calculation.

From the standard alkali, $N/10$ solutions of HCl or H_2SO_4 may be prepared in a similar manner, it being impossible to accurately weigh either of these two acids. In titrating a carbonate, if an indicator, such as phenolphthalein, which is sensitive to carbonic acid, is used, it is necessary to keep the solution at a boiling temperature or at least bring it to a boil after every addition from the burette.

VOLUMETRIC DETERMINATION OF ACETIC ACID.

As an example of acidimetry and alkalimetry, determine the strength of a sample of vinegar, as follows:

Measure accurately into a white porcelain dish of 150–250 c.c. capacity 1 c.c. of the sample. This may be measured either with a carefully graduated 1-c.c. pipette or more accurately by diluting 10 c.c. of the sample to 100 c.c. in a graduated flask, then using 10 c.c. of the dilution for the titration, the titration to be performed with $N/10$ $NaOH$, using phenolphthalein as an indicator.

The molecular weight of acetic acid is, in round numbers, 60; hence the $N/10$ factor of acetic acid will be 0.006 (acetic acid being monobasic, $HC_2H_3O_2$). To ascertain the strength of the sample of vinegar it is necessary to multiply the number of cubic centimeters used by this factor, 0.006, which will give the amount of absolute acid calculated as acetic in 1 c.c. (prac-

tically 1 gram) of the sample. Thus, if 8 c.c. of N/10 alkali were required to neutralize 1 c.c. of vinegar, multiplying the factor 0.006 by 8 would give 0.048 gram of absolute acetic acid in 1 c.c. of vinegar, which is equivalent to 4.8 per cent.

VOLUMETRIC SOLUTION OF HYDROCHLORIC ACID.

The volatile character of hydrochloric acid renders a solution of normal strength rather unstable, so decinormal or weaker solutions of this acid are commonly employed. Take a solution of hydrochloric acid which shall contain 4 to $4\frac{1}{2}$ grams per liter. Make several titrations with decinormal sodium hydroxide, and from the average of these dilute to decinormal strength as follows: the acid solution has been made rather stronger than decinormal, and therefore the 10 c.c. of dilute HCl may have required 12.5 c.c. of standard alkali for exact neutralization. In this case add 250 c.c. of distilled water to 1000 c.c. of the acid.

DETERMINATION OF MAGNESIUM HYDRATE OR MILK OF MAGNESIA.

The strength of milk of magnesia may be volumetrically determined as follows: To 5 grams of carefully mixed and accurately weighed milk of magnesia add 25 cubic centimeters of normal sulphuric acid. When dissolved, dilute the solution to 250 c.c. Mix thoroughly and titrate 25 c.c. of this solution with decinormal alkali. The result of this titration multiplied by ten will give the uncombined acid. Subtract this from the volume of standard acid originally used and calculate the amount of $\text{Mg}(\text{OH})_2$. Each cubic centimeter of the normal acid corresponds to 0.02917 gram of magnesium hydroxide.

Note. — This process is based upon the last revision of the United States Pharmacopœia, in which the term cubic centimeter is everywhere replaced by the name mils. This term indicates a milliliter or one-thousandth of a liter, which the revisers consider to be more accurate than cubic centimeter.

CARBONATE TITRATION.

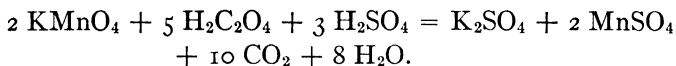
While perhaps phenolphthalein is the most serviceable of all indicators in common use, it is so sensitive to carbon dioxide that any titration which results in the liberation of CO_2 must be

modified by boiling the solution thoroughly after each addition of acid. This makes the operation somewhat tedious, but it is to be preferred to the use of other and less sensitive indicators which may not be affected by the carbon dioxide.

ANALYSIS BY OXIDATION AND REDUCTION.

DECINORMAL PERMANGANATE OF POTASSIUM.

If to a hot solution of oxalic acid containing sulphuric acid, permanganate of potash be added, the following reaction takes place:



This reaction represents a very valuable method of volumetric analysis; but, inasmuch as it is not a process of neutralization, it cannot properly come under the head of acidimetry and alkalimetry, but rather under a distinct classification, the determination involving *oxidation* and *reduction*.

Standard Permanganate Solution.—In the reaction given above we may consider that, as the molecule of $\text{K}_2\text{Mn}_2\text{O}_8$ breaks up, three of the eight atoms of oxygen are required to form the basic oxides K_2O and 2MnO (soluble in the acid as K_2SO_4 and 2MnSO_4), while the remaining five atoms are liberated and constitute the active chemical agent whereby the oxalic acid is oxidized to CO_2 and H_2O . Hence, to reduce this double molecular weight (316) to the hydrogen equivalent necessary for a normal solution, it is divided by ten (five atoms of oxygen having a valence of ten).

The Decinormal Solution may be made by dissolving 3.16 grams of pure recrystallized and thoroughly dried crystals, if they can be obtained, in distilled water, and making the solution up to 1000 c.c., or it may be standardized by titration with the N/10 oxalic acid previously prepared; in this case one would proceed as follows:

Make a solution slightly stronger than the standard required, say about 3.5 grams of the ordinary pure crystals in a liter of water; with this fill a burette, place 10 c.c. of N/10 oxalic acid

measured from a pipette in an evaporating-dish or casserole, dilute with about 50 c.c. of water, add about 10 c.c. of dilute sulphuric acid, and heat the mixture nearly to the boiling-point. Then titrate with the permanganate from the burette. The permanganate will at first be rapidly decolorized, but as the operation progresses the color fades more slowly, till at last a faint *permanent* pink color indicates that the "end point" has been reached.

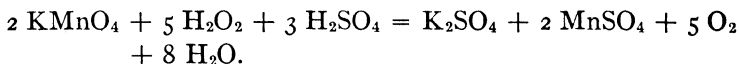
The temperature must be kept above 60° C. throughout the titration, or the oxidation will take place too slowly and an apparent end point will be obtained before the reaction is completed.

If the solution turns muddy during the operation, it is due to an insufficient amount of sulphuric acid and more should be added. The calculation is made as in the case of the N/10 NaOH described on page 148. The standard permanganate should be preserved in full, well-stoppered bottles and kept in a dark place.

It is better to have the KMnO_4 solution made up a day or two before it is standardized, thereby allowing for oxidation of traces of ammonia, etc., which the water may contain.

DETERMINATION OF PEROXIDE OF HYDROGEN.

In determining the strength of peroxide use 1 c.c. of the sample measured, as in the case of vinegar (which see), dilute with 50 c.c. of distilled water, add 10 c.c. of dilute sulphuric acid, and titrate with the permanganate in exactly the same manner as detailed in the preceding paragraph, with the exception that the titration must be made cold. The reaction takes place so easily that heat is unnecessary, and even a slight elevation of temperature may result in loss of hydrogen peroxide, the reaction in this case being as follows:



The aqueous solutions of peroxide on the market, used as antiseptics, contain about 3 per cent absolute H_2O_2 and yield approximately ten volumes of available oxygen; that is, 10 c.c.

of solution will yield 100 c.c. of oxygen. The calculation may be made to express strength of the peroxide in terms of percentage of absolute H_2O_2 by multiplying the number of cubic centimeters of $\text{N}/10 \text{ KMnO}_4$ decolorized by 1 c.c. of solution by 0.17, or to express the strength in volumes of available oxygen by multiplying the number of cubic centimeters of solution by 0.56 (more accurately 0.5594).

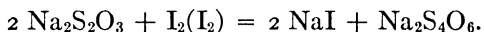
DECINORMAL IODINE.

A decinormal solution of iodine may be prepared by dissolving 12.68 grams of pure iodine crystals in one liter of water by the aid of about 18 grams of pure potassium iodide.

Iodine of sufficient purity may be obtained by carefully re-subliming selected and carefully dried crystals of so-called "chemically-pure" iodine.

DECINORMAL SODIUM THIOSULPHATE.

$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, molecular weight = 248.24. This solution may be made by weighing directly 24.824 grams of the pure crystallized salt, dissolving in water and diluting to 1000 c.c., or it may be standardized by titration with a decinormal iodine solution, the reaction being as follows:



The indicator used is a very dilute starch paste, which gives the characteristic blue color as soon as free iodine is in excess.

By means of these two standard solutions (iodine and sodium thiosulphate) a variety of determinations may be made with great accuracy. Any substance which will liberate iodine from potassium iodide may be quantitated by adding an excess of the potassium salt and titrating the free iodine with thiosulphate solution, using starch paste, as usual, for an indicator.

Peroxide of hydrogen may be thus determined as easily as by the permanganate method previously given. The process, being that of Kingzett, is given as follows by Sutton:

Mix 10 c.c. of the peroxide solution to be examined with about 31 c.c. of dilute sulphuric acid (1-2) in a beaker, adding crystals of potassium iodide in sufficient quantity. After it has stood for

five minutes, titrate the liberated iodine with N/10 thiosulphate and starch. The peroxide solution should not exceed the strength of two volumes; if stronger, it must be diluted proportionately before the analysis.

In the case of a very weak solution it will be advisable to titrate with N/100 thiosulphate.

1 c.c. N/10 thiosulphate = 0.0017 gram H_2O_2 .

Note. — The strength of metallic peroxides may be determined by acting upon the peroxide with hydrochloric acid, conducting the liberated chlorine into a potassium iodide solution and titrating the liberated iodine with standard thiosulphate.

DETERMINATION OF IODINE SOLUTION.

Titrate 10 c.c. of the iodine solution with standard sodium thiosulphate until the iodine color has become a pale yellow; then, and not until then, add the starch paste indicator and continue titration until blue color is discharged.

DETERMINATION OF HYPOCHLORITE SOLUTION.

By the use of sodium thiosulphate the strength of chlorinated lime, used as a disinfectant, may be easily determined. The following process is based upon the assay given in the nineteenth revision of the Pharmacopœia (1916).

Into a small, tared, stoppered, weighing bottle containing 10 c.c. of distilled water, introduce about 2 grams of chlorinated lime and weigh carefully. In a small mortar rub this mixture with repeated portions of water which are to be carefully transferred to a 500-c.c. graduated cylinder. When one or two hundred c.c. of water have been used in this way, rinse the weighing flask and mortar several times with distilled water, adding the rinsings to the graduated cylinder, and finally making the entire volume measure exactly 500 c.c. Mix thoroughly and allow to settle. Take 25 to 50 c.c. of this mixture, accurately measured, transfer to a porcelain dish, add half a gram of potassium iodide and 2 to 3 c.c. of acetic acid and titrate with decinormal sodium thiosulphate solution, using dilute starch solution as an indicator. Each cubic centimeter of the standard thiosulphate corresponds to 0.003546 of a gram of available chlorine.

VOLUMETRIC DETERMINATION OF ARSENIC.

Mohr's method of oxidation with iodine is a practical one. The titration is made with N/10 iodine and starch as usual, except that the solution should be at first neutral, and then about 20 c.c. of saturated solution of sodium bicarbonate should be added to every 0.1 gram of As_2O_3 supposed to be in the unknown, thus giving a certain definite alkalinity. If the solution is acid, neutralize with sodium bicarbonate, then make alkaline with more bicarbonate, as above.

VOLUMETRIC DETERMINATION OF GOLD.

While gold is usually determined quantitatively by assay in a dry way (page 163) it may be determined very accurately by titration with thiosulphate solution. Fatka (Chem. Zeit.) recommends the following process, based upon the fact that a neutral solution of gold salt with potassium iodide will give a greenish precipitate. When an excess of potassium iodide is used no precipitate is formed, but a solution of AuI_3 as AuKI_4 results. This is of a brown color and may be titrated with N/10 thiosulphate solution, whereupon the following reaction takes place:



Process: Ten c.c. of gold solution containing approximately 2 per cent of gold is treated with 4 grams of potassium iodide diluted to 100 c.c. with water and titrated with N/10 $\text{Na}_2\text{S}_2\text{O}_3$ solution, starch being used as an indicator.

VOLUMETRIC DETERMINATION OF GOLD.

(Second Method.)

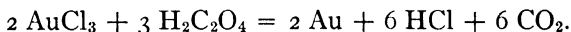
In the analysis of dental alloy, gold will remain undissolved by HNO_3 and will be weighed with the SnO_2 . It should be separated and its weight deducted before calculation is made for tin. This may be done by dissolving the gold in dilute aqua regia, evaporating the solution of gold chloride to dryness, dissolving residue in distilled water and proceeding according to

following method from Schimpf's "Manual of Volumetric Analysis."

The gold must be in the form of chloride (AuCl_3).

To the solution of gold chloride a measured excess of $\text{N}/1$ oxalic acid solution is added, and the mixture set aside for twenty-four hours.

The solution is then made up to a definite volume (say 300 c.c.). Then, by means of a pipette, 100 c.c. are removed, and the excess of oxalic found by titrating with $\text{N}/10$ permanganate in the presence of sulphuric acid. The reaction is



Each cubic centimeter of $\text{N}/1$ oxalic acid solution = 0.06523 gram of Au, or 0.1004 gram of AuCl_3 .

ANALYSIS BY PRECIPITATION.

Because certain elements possess a selective affinity for other elements, it is possible to determine many substances quantitatively by precipitation. That is, if silver nitrate is added to a mixture of a soluble chloride and a chromate, the chlorine will combine first with the silver, forming AgCl , to the exclusion of the chromate. After the last trace of chlorine has been so combined, the silver chromate, a salt with an intense red color, will be formed; hence it is possible to determine the strength of solutions of soluble chlorides by titration with standard AgNO_3 , using potassium chromate as an indicator. This process is used in analysis of drinking-water, of saliva, and of urine, but for each of these it is desirable to have solutions of special strength.

A DECINORMAL SILVER SOLUTION

may be made by dissolving seventeen grams of pure crystallized AgNO_3 in a liter of distilled water, and with this a

DECINORMAL SODIUM CHLORIDE SOLUTION

may be prepared as follows:

Weigh out 6 grams of the purest salt obtainable and dissolve in approximately 1 liter of distilled water. With a pipette, measure 10 c.c. of this solution into a white porcelain dish, dilute

to about 20 c.c. with H_2O , add 2 to 5 drops of neutral potassium chromate (K_2CrO_4) and add AgNO_3 from a burette till a faint pink color *persists*.

The calculation and dilution is made exactly as described on page 148 in the preparation of a standard NaOH solution. The silver nitrate solution used to determine chlorine in urine may be given such a strength that 1 c.c. precipitates just 10 milligrams of sodium chloride. This is equivalent to 0.006065 gram of chlorine. A solution of this strength is produced when 29.075 grams of pure, fused silver nitrate are dissolved in sufficient distilled water to measure 1 liter of solution. If chlorine is to be determined in drinking-water, it is usually necessary to concentrate the water to at least one-fifth its bulk and then to use not more than 1 or 2 drops of neutral chromate as indicator. The standard silver nitrate for this titration should be very dilute. A convenient solution may be prepared by diluting the standard AgNO_3 for urine 1 to 10. In saliva the sample may be diluted with an equal volume of water and titrated as in the case of drinking-water. In all quantitative processes where silver chromate is used to determine the end point, the solution must be practically neutral, as the formation of this salt is prevented by either acids or alkalies.

DECINORMAL POTASSIUM SULPHO-CYANATE.

This solution may be made in a manner similar to that previously described for the preparation of standard sodium chloride solution, except that a fairly strong solution of ferric alum should be used as indicator and the titrated solution should contain moderate excess of nitric acid.

DETERMINATION OF SILVER BY SODIUM CHLORIDE SOLUTION.

The strength of neutral silver solutions may be determined by the use of decinormal sodium chloride, with yellow potassium chromate as an indicator. It is better to add the silver solution from the burette, as the precipitate of silver chromate, which would be formed by adding the indicator to the silver solution, disintegrates with difficulty.

DETERMINATION OF SILVER BY POTASSIUM SULPHOCYANATE SOLUTION.

Silver may be determined volumetrically in nitric acid solution by titration with standard KCNS solution, with ferric alum as an indicator. The sulphocyanate solution must be standardized against decinormal AgNO_3 as follows: Prepare a solution containing not less than 10 grams of chemically pure KCNS per liter. Place this solution in the burette and put in the porcelain dish 10 c.c. of decinormal AgNO_3 which has been strongly acidified with nitric acid and 15 or 20 drops of a solution of ferric alum, added as an indicator. The end point is indicated by the faint red color of ferric sulphocyanate, produced by the first excess of KCNS. The calculation will be the same as previously described in the preparation of N/10 NaOH (page 148).

DETERMINATION OF CHLORINE.

Chlorine may be determined by titrating 10 c.c. of solution with N/10 silver nitrate, potassium chromate being used as an indicator. When sufficient silver nitrate has been added to precipitate all of the chlorine as silver chloride any additional silver nitrate will react with the chromate present and a red precipitate of silver chromate will be formed. The end point is determined then by the appearance of a *permanent* red tinge to the precipitate.

A determination of chlorine of greater accuracy for physiological work when phosphates are present may be made indirectly by taking 10 c.c. of solution, acidifying quite strongly with nitric acid, then adding 20 c.c. of N/10 silver nitrate and titrating with N/10 potassium thiocyanate using *ferric alum* as an indicator. The presence of nitric acid dissolves any phosphates or urates which may be present.

Since in this determination it is the *excess* only of silver nitrate which is titrated with the sulphocyanate the calculation differs slightly from a direct titration. Subtract the number of c.c. of sulphocyanate used from the amount of silver nitrate originally added, i.e. 20 c.c., and multiply the difference by .00355, the

N/10 factor for chlorine. This gives the weight of chlorine in the amount of solution taken, i.e. 10 c.c. To obtain per cent multiply by 10.

VOLUMETRIC DETERMINATION OF COPPER.

Into a solution of copper, free from other metals of Group I or II, pass H_2S gas. Wash the resulting copper sulphide thoroughly with H_2S water, and dissolve in dilute nitric acid; then wash the paper in warm water, add to the filtrate (wash-water) sodium carbonate until precipitate formed is nearly dissolved; then add 1 c.c. of dilute NH_4OH . Titrate, to complete disappearance of blue color, with KCN solution previously standardized, after this same method, against pure copper wire. A little practice is required in determining the end point, to give the process any degree of accuracy. An excess of ammonia should be avoided, as it interferes with the accuracy of the end point.

VOLUMETRIC DETERMINATION OF ZINC.

(For use in analysis of amalgam alloys.)

Concentrate the solution from which silver and copper have been removed, together with all wash-water; if it is acid in reaction, evaporate it to dryness, and dissolve the residue in water; then add a fairly strong solution of oxalic acid and an equal volume of strong alcohol. Allow to stand fifteen to thirty minutes, filter, and wash with 70 per cent alcohol till oxalic acid is removed; dry until the alcohol has disappeared, dissolve in dilute sulphuric acid, and titrate the solution with N/10 permanganate, and calculate the zinc from the amount of oxalic acid found.

This method is usually fully as satisfactory as the gravimetric determination given on page 162.

VOLUMETRIC DETERMINATION OF CALCIUM.

This method is based upon that recommended by Dr. Percy R. Howe, *Dental Cosmos*, April, 1912. To 5 c.c. of solution, add as much more distilled water and a slight excess of oxalic acid

or ammonium oxalate (5 c.c. of normal solution will be sufficient). Add ammonium water to alkaline reaction, heat nearly to the boiling-point, and allow to stand for twenty to thirty minutes. Filter through a hardened filter paper into a small beaker which is allowed to stand on a piece of black glazed paper. Under these circumstances, a slight rotary motion of the beaker will show if any of the white precipitate of calcium oxalate is passing through the paper.

After filtration is complete, wash five times in hot distilled water; then place the precipitate, together with the paper, into a small beaker, add about 30 c.c. of dilute sulphuric acid, and heat nearly to the boiling-point; then titrate with N/20 permanganate solution.

G. W. Clark, in an article on micro-methods for the determination of calcium in the *Journal of Biological Chemistry*, Dec., 1921, showed that "the direct determination of calcium in the blood is accurate to ± 5 per cent and equal in this respect to any of the numerous micro-methods found in the literature."

Dr. Clark has also shown that it is desirable to thoroughly centrifuge the precipitate in an ordinary electric centrifuge with a speed of 1800 revolutions per minute and that the hydrogen-ion concentration best suited for the precipitation of calcium is practically that of N/1 sulphuric acid. Hence, a modification of the method given on the preceding page is recommended for use in saliva analysis, as found in Vol. II.

DETERMINATION OF PHOSPHATES.

Instead of determining phosphates with the usual standard solutions a special solution of uranium acetate or uranium nitrate is usually used made of such a strength that 1 c.c. is equivalent to 5 mg. of phosphate. The method of preparation is as follows:

Dissolve 35.5 grams of pure uranium nitrate or acetate in about 800 c.c. of distilled water; add three or four c.c. of glacial acetic acid and heat it enough to complete solution. Allow to stand overnight, filter carefully, and make up to 1000 c.c. Standardize this solution against crystallized microcosmic salt by dissolving 14.721 grams of the pure salt ($\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$)

in sufficient water to make 1000 c.c. Then titrate 20 c.c. of this solution, to which has been added 30 c.c. of water and 5 c.c. of sodium acetate solution, with the uranium solution (method of titration is given under process below).

The uranium solution should then be adjusted (diluted) so that it will take exactly 20 c.c. for this titration, when one c.c. of the uranium will be equivalent to five milligrams of P_2O_5 .

The sodium acetate solution referred to contains 100 c.c. of 30 per cent acetic acid and 100 grams of sodium acetate in enough distilled water to make 1000 c.c.

Method of Titration. — Take 10 c.c. unknown phosphate solution and add 5 c.c. of sodium acetate.

Titrate, while hot (80° or above), with the standard uranium solution till a drop of the mixture placed on a white porcelain tile with a drop of the indicator $\text{K}_4\text{Fe}(\text{CN})_6$ gives a distinct brown color. This method of determining the end point is known as "spotting" and with a little practice gives very accurate results.

The number of cubic centimeters of uranium solution multiplied by 5 gives the weight of phosphate in mg. in the 10 c.c. of solution started with.

If the "spotting" method for obtaining the end point seems undesirable *cochineal* may be used as an indicator. The end-point is reached when the red color changes to green. The spotting method is the more accurate for real quantitative work but the use of cochineal is simpler and sufficiently accurate for many determinations.

GRAVIMETRIC DETERMINATIONS.

Gravimetric determinations are, as a rule, more accurate than volumetric; but they require greater care and attention to details, and are therefore less satisfactory in the hands of the beginner. Some determinations, however, on account of difficulties in obtaining accurate end-points and absolute separations, are really easier when made by gravimetric processes. A few of these will be given.

GRAVIMETRIC DETERMINATION OF TIN AS SnO_2 .

Tin may be separated from dental alloys, in the absence of gold or platinum, by simply dissolving the alloy in nitric acid. Tin will remain as a white insoluble metastannic acid. As stated on page 102, metastannic acid, upon long standing, will change to somewhat soluble compounds; hence this operation should be completed with reasonable rapidity. After complete disintegration of the alloy, the insoluble tin compound may be separated by filtration through asbestos fiber, contained in a Gooch crucible. The method of procedure is as follows:

A little fine asbestos fiber, washed in acid and held in suspension in water, is placed on the bottom of the crucible. The crucible is then placed in the top of a filtering flask, from which the air is exhausted by the suction pump. This packs the asbestos down firmly on the bottom of the crucible in a thin layer. Care should be taken that the quantity of asbestos used is such that water will pass through it easily. The crucible with asbestos is next dried, ignited, and weighed. Now transfer the precipitate of tin oxide (metastannic acid) to the crucible, taking care that none is lost, and wash thoroughly six or eight times, then dry, ignite strongly, and weigh again.

If the ignited residue, weighed as tin oxide, does not contain gold or platinum, the weight of tin may be obtained by multiplying the weight of the ash by 0.788.

GRAVIMETRIC DETERMINATION OF SILVER.

The gravimetric determination of silver is not difficult, and is rather more accurate than the volumetric method. The silver is obtained in the form of silver chloride. This is separated by filtration through an ashless paper, and dried. Then the dried precipitate is transferred, as completely as possible, to a square of black glazed paper, and preserved under a funnel or bell glass. The filter paper, containing traces of silver chloride which could not be removed, is next incinerated in a previously weighed porcelain crucible.

As slight reduction of silver chloride to silver may take place during the ignition of the paper, it is necessary to add, after the

paper is completely burned, a drop or two of nitric acid, and after the excess has been driven off by gentle heat, a drop or two of hydrochloric acid. This treatment dissolves any reduced silver and precipitates silver chloride. After careful heating, to dry the precipitate in the crucible, the reserved portion of silver chloride is carefully brushed into the crucible, and the whole ignited until the silver chloride begins to fuse. It is then cooled and weighed as silver chloride.

GRAVIMETRIC DETERMINATION OF COPPER.

Copper may be determined quite easily by electrolysis of the faintly acid (H_2SO_4) solution. The copper solution must be freed from other metals and preferably be obtained as a solution of copper sulphate of approximately 0.1 of 1 per cent of copper. Fifty c.c. of such a solution are put into a platinum dish, which is placed upon a copper plate connected with the negative pole of a battery. A strip of platinum suspended from the positive pole is immersed in the solution, and the current is allowed to pass for three to twelve hours, according to the strength of the copper solution. The ordinary 110-volt (direct) current, employed for electric lighting, may be used by introducing a resistance of three to six 40-watt lamps. After the copper has been entirely deposited, the residual solution is drained out of the platinum dish; then a little alcohol is added and is also drained out; the last traces of alcohol are then ignited, and the precipitated copper is thus dried and left in condition to weigh. Care must be taken to avoid oxidation of the finely-divided copper; if it turns black too much heat has been used and partial oxidation has taken place, which has, of course, resulted in an increase of weight.

GRAVIMETRIC DETERMINATION OF ZINC.

Zinc may be determined gravimetrically by precipitation as zinc sulphide, as follows: To a measured portion of the solution, free from all metals (except zinc) of Groups I, II, III, and IV, add ammonium chloride, ammonium hydroxide, and ammonium sulphide, as in qualitative analysis. Filter the precipitated zinc sulphide on to counterpoised filters, wash thoroughly with

water containing a little ammonium sulphide, dry in an atmosphere free from oxygen (hydrogen or hydrogen sulphide), and weigh as zinc sulphide.

GRAVIMETRIC ASSAY OF GOLD AND SILVER IN THE DRY WAY.

It is often more convenient to determine gold and silver by the fire assay than by the volumetric methods previously given. This is usually accomplished by fusion with an excess of lead and a borax flux. The mixture is kept at a high heat for upwards of thirty minutes, with a current of air passing over the surface of the molten metals. This serves to oxidize and carry away the baser metals, leaving the gold and silver with but a slight amount of lead, possibly a trace of copper and tin. The purification is completed by cupellation. When the traces of lead and other metals are absorbed by the cupel or are driven off as volatile oxides, the button of gold and silver is next cooled *very slowly* and carefully weighed. From this the silver may be dissolved by nitric acid, unless the gold is in considerable excess, which would rarely be the case. If it happens that the gold is present in sufficient quantity to prevent the solution of the silver in nitric acid, a known weight of pure silver may be added in amount sufficient to increase the percentage of silver to 75 or over. After this has been fused, all the silver is dissolved out with nitric acid, leaving the gold.

The gold which has resisted solution may be found as small black particles or grains in the bottom of the crucible. This should be carefully washed with distilled water by decantation, very carefully dried and brought to a red heat, which will give a button of pure gold. This may be weighed and the weight subtracted from the weight of gold and silver button previously obtained.

QUANTITATIVE ANALYSIS OF DENTAL ALLOYS CONTAINING Au, Sn, Ag, Cu, Zn.

Weigh accurately 0.5 gram of alloy which has been reduced to fine filings and from which all particles of iron have been carefully removed by a magnet, transfer to a beaker, and dissolve in

15 c.c. of strong HNO_3 and 10 c.c. of H_2O , by aid of gentle heat. If the sample contains tin or gold, complete solution will not be effected; but, by watching the character of the sediment through the bottom of the beaker, it is easily possible to determine when the alloy has been completely disintegrated.

If silver is to be determined by titration with NaCl and K_2CrO_4 , evaporate on a water-bath till all nitric acid has been expelled.

If silver is to be determined by the sulphocyanate solution, evaporation at this point is not necessary. In either case, make the whole solution up to 250 c.c. with distilled water; then filter out tin and gold, following the method given under gravimetric determination of tin (page 161), reserving the filtrate before any wash-water has been added. For convenience, this filtrate may be marked "A." Titrate this filtrate ("A") for silver as follows:

Take a measured volume, about 30 c.c., and place in a porcelain dish, with ferric alum as indicator.

Then place the standard KCNS in the burette and titrate till the faint red color is produced.

Suppose 8 c.c. of KCNS is used. The weight of silver in 1 c.c. of a decinormal solution is 0.0108 gram. Multiplying 8 by 0.0108 = 0.0864. Divide by number of cubic centimeters of solution taken, $0.0864 \div 30 = 0.00288$ gram Ag in 1 c.c. of solution.

Multiply by whole number of cubic centimeters and divide by weight of alloy taken, and result will be percentage of silver.

Take 100 c.c. of filtrate "A," and precipitate silver by slight excess of HCl . Filter and wash precipitate thoroughly with warm water. Concentrate filtrate and wash-water, which may be designated as filtrate "B." Pass H_2S gas into "B" till copper is entirely separated as CuS . Filter and wash CuS seven or eight times with dilute H_2S water. Reserve filtrate and wash-water as filtrate "C." Dissolve CuS in dilute HNO_3 , wash paper carefully, concentrate, and determine amount of copper by deposition upon platinum (page 162). Concentrate filtrate "C" and determine zinc by volumetric method given on

page 158. Gold and tin, in residue insoluble in nitric acid, may be determined by method given on pages 154 and 161.

QUESTIONS IN VOLUMETRIC WORK.

Why is an N/10 solution of hydrochloric acid more generally serviceable than a similar solution of oxalic acid?

Why use nitric acid for titration of chlorine in urine by means of KCNS?

EXPERIMENTS.

REVIEW EXPERIMENTS.

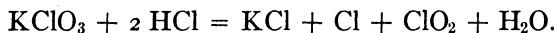
Note. — A few review experiments and problems of special value, from the dental standpoint, have been introduced, as an aid to students who have not had their prerequisite Chemistry during the *year previous* to their entrance into the dental school.

Oxidation and Valence.

Exp. 1. Carefully weigh a porcelain crucible. Then weigh into it about 1 gram of clean copper turnings. Heat strongly for about fifteen minutes; then cool and weigh. Explain increase of weight and compare result obtained with theoretical result, assuming that the entire amount of copper has been oxidized.

Exp. 2. To a solution of potassium chlorate add a little sulphurous acid and boil. Test the sulphurous acid for sulphuric acid (H_2SO_4) before starting and after completing the experiment.

Exp. 3. Prepare some chlorine water as follows: Into a test-tube drop some crystals of KClO_3 . Add a few c.c. of strong HCl , just enough to cover the crystals. Allow the evolution of gas to become fairly brisk, and fill tube three-quarters full of water.



Caution. Avoid heating, as oxides of chlorine are formed in this reaction and are liable to explode if heated.

Avoid the escape of Cl gas into the laboratory, as far as possible.

Exp. 4. Warm a little sulphurous acid solution with a few drops of the chlorine water just prepared, testing for H_2SO_4 as in Exp. 2.

Exp. 5. To a dilute solution of potassium ferrocyanide add some strong chlorine water, and warm. After ten or fifteen

minutes, test for the presence of ferrocyanide with dilute ferric chloride. Explain.

Peroxides.

Exp. 6. Prepare a solution of peroxide of hydrogen as follows: Add to 10 or 15 grams of BaO_2 enough water to make a paste and allow to stand about half an hour. Then add 20 or 30 c.c. of a 10 per cent solution of H_2SO_4 . Stir thoroughly and after five minutes filter off the solution and test for H_2O_2 .

The half-hour treatment with water serves to hydrate the BaO_2 and makes the action of the acid much more rapid.

What is the white solid remaining on the filter paper?

Complete $\text{BaO}_2 + \text{H}_2\text{SO}_4 =$

Exp. 7. Test the filtered solution of H_2O_2 from preceding experiment as follows: In a test-tube, acidulate a small quantity of the liquid with a few drops of H_2SO_4 . Add a small quantity of ether and 5 or 6 drops of K_2CrO_4 solution. Shake well. The H_2O_2 gives a blue color which is absorbed by the ether.

Exp. 8. Dissolve peroxide of sodium in dilute HCl , leaving the reaction faintly acid. Dissolve also a little peroxide of sodium in water and compare the bleaching properties of the two solutions.

Exp. 9. To a solution of H_2O_2 add a little KI solution, then add about 5 c.c. of chloroform. Shake well. Set aside for a few moments, then examine and explain result.]

Exp. 10. Dissolve a very little sodium perborate, $\text{NaBO}_3 \cdot 4 \text{H}_2\text{O}$, in a little *warm* water and test the solution for H_2O_2 with potassium bichromate, sulphuric acid and ether, as in Exp. 7.

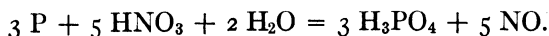
Oxides and Oxyacids of Chlorine and Phosphorus.

Exp. 11. HClO . Compare properties of chlorides, hypochlorites and chlorates as follows: Test a 3-5 per cent water solution of NaCl , NaClO , and KClO_3 by adding to each, in separate test-tubes, a little AgNO_3 .

Exp. 12. In like manner test each of above solutions by adding a little KI solution, then a little starch paste.

Exp. 13. Place a little red phosphorus in a porcelain capsule

and add a little nitric acid. Heat gently till the phosphorus disappears. Save the solution. Phosphoric acid is formed by this experiment, as follows:



Exp. 14. Take two test-tubes; into one put a little of the phosphoric acid solution made in Exp. 13, and into the second, a solution of sodium phosphate (Na_2HPO_4) from the desk bottle; then add to each about 5 c.c. of ammonium molybdate solution in HNO_3 .

Exp. 15. Repeat Exp. 14, using magnesium mixture in place of the ammonium molybdate. This may or may not give a precipitate with the acid solution. Explain why it may not.

Exp. 16. To a sodium phosphate solution add a solution of silver nitrate. Filter and test solubility of the precipitate in HNO_3 . What is the precipitate? How does it differ from AgCl ?

Exp. 17. To some sodium phosphate add a solution of BaCl_2 . Filter and test solubility of precipitate in HCl . Write reaction.

Exp. 18. Prepare some sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) by heating in a porcelain crucible Na_2HPO_4 , till a little of it dissolved in H_2O fails to give a yellow precipitate with silver nitrate.

Boric Acid.

Exp. 19. Make a hot strong solution of borax ($\text{Na}_2\text{B}_4\text{O}_7$), filter while still hot and add to the clear filtrate a few c.c. of concentrated HCl . Crystals of boric acid will separate as the mixture cools, if not at once. Complete reaction.



Exp. 20. To a little borax in a small porcelain dish add a few drops of strong H_2SO_4 and about 5 c.c. of alcohol. Set dish in fairly dark place and set fire to the alcohol; watch color of flame, till alcohol is used up. Repeat the experiment *without* the sulphuric acid. Explain difference in results.

MIGRATION OF IONS AND IONIZATION.

Exp. 21. Half fill four test-tubes with hot 3 per cent gelatine solution and allow it to congeal. Label and number the test-tubes and then nearly fill them with solutions named below.

- (a) 1 per cent solution Congo red
- (b) 1 per cent solution picric acid
- (c) 2 per cent aqueous solution copper sulphate
- (d) colloidal silver solution.

Compare the diffusion in the different tubes.

Exp. 22. Fill a U-tube half full of a 5 per cent agar-agar solution with sufficient copper sulphate to produce a distinct blue color. Set aside for agar-agar to congeal. Mark the level of the agar on the outside of the tube with a grease pencil, and add a little potassium nitrate solution and agar-agar to each side of the tube, and then a little plain potassium nitrate. Introduce electrodes and pass electric current for about half an hour. Note carefully the appearance of each leg of the U-tube, and explain.

Exp. 23. Carefully neutralize 25 c.c. of HCl (desk reagent) with dilute NaOH, until resulting mixture has practically no effect on litmus paper.

Take 10 c.c. of neutralized solution and dilute to 100 c.c. Label dilution "Solution 1." In each of two evaporating dishes place 10 c.c. of Solution 1. To one add phenolphthalein as indicator, to the other methyl red. Neutralize each a second time by use of $N/40$ NaOH or $N/40$ HCl from burette. Note the amount of acid or alkali used.

Determine hydrogen-ion concentration of Solution I.

Exp. 24. To 50 c.c. of a dilute solution of methyl orange in each of three beakers, add 5 c.c. of 1 molar acetic acid. To one of the solutions add some solid sodium chloride (about 6 grams added in 2 or 3 portions). To the second solution add some cane sugar. Compare the colors produced with the third solution, which is used as a control, and also with a solution containing only methyl orange and sodium chloride. What causes the

increased intensity in color in one tube? Conclusion as to effect of presence of *foreign salts* on ionization of weak acids.

Exp. 25. To 5 c.c. of a tenth-molar solution of ferric chloride add 15 c.c. of a tenth-molar solution of KCNS. Dilute a portion of the red solution thus produced with distilled water, until only a faint yellow color remains. Divide this nearly colorless solution into four parts. To one add 2 or 3 c.c. of ferric chloride, to the second, about twice as much of the KCNS originally used, to the third, add one-half its volume of $M/10$ solution of KCl.

Compare portions 1 and 2 and explain how this experiment shows the law of chemical equilibrium.

Explain how it illustrates ionization of ferric sulphocyanate and why it is necessary to use more of the KCNS than of the $FeCl_3$ solution to get approximately the same depth of color.

Now compare 3 and 4 and explain how these solutions show the reversible character of the reaction between $FeCl_3$ and KCNS. Do portions 3 and 4 illustrate law of mass action?

Exp. 26. To two of three portions of a dilute solution of methyl orange, equal quantities of acetic acid (5 c.c. molar acid) are added, the third portion being reserved to show the color of the neutral solution of the indicator. Now, into one of the solutions containing the acid, gradually drop a few crystals of sodium acetate. Note the color produced and compare with that of the original neutral solution. Explain on basis of repression of ions. Test acidity of solution to which salt has been added, with litmus. Explain. Which indicator is more sensitive to the hydrogen ion? What effect does the presence of a salt of a weak acid have on that acid?

OSMOSIS AND DIALYSIS.

Exp. 27. In a dialyzing tube place a solution of NaCl. In another dialyzing tube place a solution of egg albumin; set the tubes in separate small beakers of distilled water. After they have stood for several hours, test the distilled water in the first beaker for salt, by adding a little silver nitrate solution, and test the water in the second beaker for albumin, by boiling with a

drop of acetic acid. Compare results of these tests with similar tests made with known solutions of salt and of albumin.

Exp. 28. Tie a small dialyzing sac or parchment tightly to a piece of glass tubing 4 or 5 inches long with an internal diameter of 3 or 4 millimeters.

Fill the sac with sugar solution and then introduce a previously selected capillary tube which fits into the larger tube rather closely. Seal joints with paraffin and suspend the sac in a beaker of distilled water. Allow to stand several hours. Watch the level of the liquid in the capillary tube and explain results.

HYDROLYSIS.

Exp. 29. Rose's Reaction. — Color a solution of borax, (M/10) with litmus solution, then add acetic acid very carefully till the litmus just turns pink. Now dilute largely by turning into distilled water. The color again becomes blue, owing to increased hydrolyzation of the borax.

Exp. 30. Place 2 c.c. of M/10 solution of borax in each of two small beakers, add to one a few drops of HgNO_3 , and to the other a few drops of AgNO_3 solution. Note color of the precipitate in each case.

In each of two larger beakers place 50 c.c. of water with 5 or 6 drops ($\frac{1}{2}$ c.c.) of the above borax solution; then to one add a few drops of HgNO_3 solution, and to the other some AgNO_3 solution, till a precipitate is produced. Note color of precipitate in each case. (Hg_2O and Ag_2O are produced.)

Now dilute the mixture in the first two beakers (containing precipitate of borates) with 50 c.c. of water. Stir and allow to stand ten minutes. Draw inference regarding hydrolysis of borax, also regarding relative stability of the borates of silver and mercury.

COLLOIDS.

Exp. 31. To about 10 c.c. of ferric chloride solution add ammonium hydroxide, drop by drop and with constant stirring, till a decided permanent precipitate is obtained, with reaction remaining acid. Filter. Take three separate test-tubes, each

one-fourth full of distilled water; to one add 4 drops of filtrate, to the second add 4 drops of the filtrate and a few c.c. of ammonium chloride solution, and to the third add about 4 c.c. of the filtrate. Then make all three tubes faintly alkaline with ammonium hydroxide. Filter again and test each filtrate for iron by acidifying with hydrochloric acid and adding ferrocyanide or potassium thiocyanate. One tube should give positive results, the others negative. Explain.

Exp. 32. Pass hydrogen sulphide into about 5 c.c. of an aqueous solution of arsenious oxide. Note color. Can a precipitate be detected? Prove that this is not a case of supersaturation, by adding to a small portion a little solid arsenious sulphide; this will cause no precipitation. What conclusion do you reach in regard to the condition of the arsenious sulphide?

Save solution.

Precipitation of Colloids.

Exp. 33. To part of the solution of arsenious sulphide prepared in Exp. 32, add some hydrochloric acid or sodium chloride. What is the result? Which ion produces the precipitate? What is your conclusion as to the effect of electrolyte on colloidal solution? How would this effect analytical work?

Exp. 34. In each of three test-tubes or beakers put 15 c.c. of the colloidal solution of As_2S_3 . To one add ammonium nitrate solution, to the second magnesium nitrate solution, and to the third aluminium nitrate solution, and note the *number of drops* necessary to produce complete precipitation in each case. What is your conclusion as to influence of valence on the precipitating power of electrolytes.

What result do you think an increase of the valence of the *negative* ion would have, knowing that colloidal arsenious sulphide carries a negative charge?

Protective Colloids.

Exp. 35. Mix together in a test-tube some M/10 solution silver nitrate and dilute hydrochloric acid. In another test-tube mix some solutions of silver nitrate and hydrochloric acid,

each of which contains 1 per cent gelatine. Try filtering the solution.

If the reaction between silver nitrate and hydrochloric acid is a test for silver, would the presence of a *protective colloid* like gelatin interfere in obtaining the test?

PRECIPITATION.

Exp. 36. Influence of Temperature.

(a) In each of two test-tubes put about 5 c.c. of 1 per cent lead nitrate solution. Heat one of the test-tubes to the boiling point and submerge the other one in ice water. Then add a few c.c. of dilute hydrochloric acid to each. State and explain the result.

Exp. 37. Influence of Solvent.

(a) To a few c.c. of a solution of barium chloride add several c.c. of concentrated hydrochloric acid. What is the result?

(b) To concentrated hydrochloric acid add a strong solution of sodium chloride. Explain precipitation.

(c) To 5 c.c. of an alcoholic solution of naphthalene add an excess of water.

Exp. 38. Influence of Concentration.

(a) To a few c.c. of strong hydrochloric acid add a few drops of silver nitrate.

(b) To a few c.c. of dilute hydrochloric acid add a few drops of silver nitrate.

(c) Take 5 or 10 c.c. of dilute sulphuric acid and add 1 per cent lead nitrate, drop by drop, until precipitation occurs. Note the number of drops necessary to produce cloudiness.

Exp. 39. Influence of Solubilities.

(a) To a mixture of copper sulphate and cadmium sulphate add hydrogen sulphide water, and filter.

To the filtrate add more hydrogen sulphide water, and filter again if precipitate forms. Repeat until no further precipitation occurs. Which is the more soluble, cadmium sulphide or copper sulphide? What precaution must be used in precipitating these two metals if occurring together in solution?

(b) Take a hydrochloric acid solution of cadmium sulphate

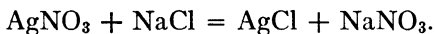
and divide in two parts. To one add ammonium hydroxide until only faintly acid. Then to each add hydrogen sulphide water. What is the result?

LABORATORY WORK IN QUALITATIVE ANALYSIS.

During the study of qualitative analysis the preliminary work for each group, which may consist in confirming the statements given in the text regarding the formation of precipitates and properties of the same, should be carried out prior to the analyses of unknown solutions.

EXPERIMENTS WITH METALS.

Exp. 40. Precipitate a little silver chloride according to the following:



Filter, and allow the precipitate to become nearly dry. Mix a little of the precipitate with powdered charcoal, and heat before the blowpipe until a globule of metallic silver is obtained.

Exp. 41. Mix intimately a small quantity of litharge and powdered charcoal. Heat in a blowpipe flame and obtain a particle of metallic lead.

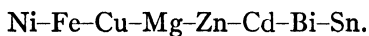
Exp. 42. In a solution of lead (acetate or nitrate) suspend a strip of zinc. Set aside for several hours and note the separation of metallic lead. Write the reaction.

Exp. 43. Put a small quantity of cinnabar (HgS) into a small, hard glass tube open at both ends. Hold the tube, slightly inclined, in a strong heat of the Bunsen flame; then examine the sublimate under the microscope. What becomes of the sulphur?

Exp. 44. In an open, hard glass tube, heat strongly a mixture of charcoal and copper oxide. Explain the change of color.

Exp. 45. To a very small piece of copper foil in a test-tube, add a little ammonium chloride solution and allow to stand.

Exp. 46. Heat, in forceps or on triangle, a very small piece of each of the following metals, allowing each to fall, as it melts, on a smooth cold slab (cement floor will do). Return melted metals to office for credit.



Study table of melting-points and write your conclusions regarding the temperature of the Bunsen flame.

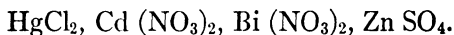
Exp. 47. Fill each of three test-tubes half full of a solution of CuSO_4 . Suspend in the first a knife blade; in the second, a strip of clean metallic zinc; in the third, a strip of magnesium ribbon. Write reactions.

Exp. 48. Warm gently in a test-tube a little MnO_2 and HCl . Write reactions. Repeat with PbO_2 and HCl ; with PbO and HCl . Explain differences in action of the metallic oxides.

Exp. 49. Suspend a piece of thin sheet copper in an $\text{N}/5$ solution of AgNO_3 . Allow the deposit to become fairly thick, and examine to see if it is strongly adherent. Dilute this same silver solution with about three times its volume of water, and again immerse a strip of copper. Allow to stand several minutes, remove, wash carefully, dry by gentle heat and then heat strongly in a Bunsen flame. Determine whether the silver coating will take a polish.

Exp. 50. Immerse strips of metals in the designated solutions. If no action takes place, transfer to a porcelain dish and heat.

Cu in each of the following



Repeat using Zn in place of Cu.

"	"	Ni	"	"
"	"	Mg	"	"

Do your results follow the table given on page 95 ?

Exp. 51. Construct a small galvanic battery as suggested on page 96, using lead as one permanent electrode and varying the other one, using Zn, Cu, Sn and Ag. Connect the electrodes with a galvanometer and watch the direction of the current.

APPENDIX.

REAGENTS.

It is desirable that all reagents be made with reference to the molecular weights of the substances employed. These may be from one to ten times the molecular weight per liter, while the solutions for practice are from one-tenth to one-fourth the molecular weight per liter. Salt solutions used as reagents are conveniently from five to ten per cent; that is, a molar concentration is selected bringing the strength within these limits.

In the following list a few exceptions will be noted.

Acetic Acid.— desk reagent — glacial acetic acid one part, distilled water four parts.

Ammonia (dilute).— Strong ammonia one part, distilled water two parts.

Ammonium Carbonate, 2M; 157 grams of commercial ammonium carbonate are dissolved by the aid of heat in about 900 c.c. water. After this has become cold add 75 c.c. of concentrated ammonium hydroxide, and make up volume to one liter.

Ammonium Chloride, 4M, or about a twenty per cent solution.

Ammonium Molybdate Solution for Phosphates. — This may be made by dissolving twenty grams of ammonium molybdate in a mixture of 250 c.c. NH_4OH and 250 c.c. of water. Then this solution is added to 1000 c.c. of nitric acid making 1500 c.c. of reagent. In using this solution as a test for phosphates it is necessary to heat the mixture to about 60°C .

If the reagent is prepared as follows it reacts without heating, is more sensitive than that produced by the first formula and is recommended as the better of the two. Dissolve 100 grams of

molybdenum trioxide (molybdic acid) in 400 c.c. of dilute NH_4OH (10 per cent). Allow to cool and add all at once 1000 c.c. of dilute HNO_3 (HNO_3 three parts, H_2O two parts). The precipitate first formed is immediately redissolved and the product should be a perfectly clear, nearly colorless solution.

Ammonium Oxalate, M/4, 35.52 grams per liter.

Ammonium Sulphide. — Saturate 300 c.c. of strong ammonia with hydrogen sulphide gas. Then add an equal volume of strong ammonia and sufficient water to make 1000 c.c. In this solution dissolve one or two grams of sulphur, giving the yellow ammonium sulphide (polysulphide).

Cochineal. — For use in phosphate titrations — extract cochineal with 30 to 50% alcohol and filter.

Ferric Alum. — For use in silver and chlorine determinations.

A saturated aqueous solution to which sufficient strong nitric acid is added to make about a 10% solution.

Ferric Chloride. — 2.5 per cent solution acidified with HCl .

Gram's Solution: See Iodine solutions.

Hydrochloric Acid (dilute). — Hydrochloric acid, strong, (sp. gr. 1.20) one part; distilled water, two parts.

Iodine Solution. — 10 grams iodine, 20 grams KI , made up with water to one liter.

Lugol's solution is iodine five grams, potassium iodide ten grams, and sufficient distilled water to make one hundred grams. (U. S. P.)

Gram's solution: Iodine one gram, potassium iodide two grams, and sufficient distilled water to make two hundred grams.

Lugol's Solution. — See Iodine.

Magnesia Mixture. — 125 grams of ammonium chloride, 125 grams of magnesium sulphate, dissolved in sufficient water to make one liter of solution, then add 125 c.c. of strong ammonia water.

Mercuric Chloride Solution. — Five per cent HgCl_2 in distilled water.

Nitric Acid (dilute). — Strong HNO_3 (sp. gr., 1.42) one part, and water three parts.

Potassium Ferricyanide Solution is unstable and should freshly prepared each time it is used.

Potassium Ferrocyanide Solution. — $\text{K}_4\text{Fe}(\text{CN})_6$ one-fourth molar solution (9.2 per cent).

Potassium Sulphate. — A 10 per cent solution in distilled water.

Potassium Sulphocyanate. — A 5 per cent solution in distilled water.

Silver Nitrate. — A $2\frac{1}{2}$ per cent solution in distilled water.

Sodium Hydroxide. — A 10 per cent solution in distilled water.

Sodium Phosphate. — Na_2HPO_4 . — A 7 per-cent solution in distilled water.

Starch Paste (thin). — Rub about one-half gram of starch to a thin paste with cold water. Add sufficient boiling water to dissolve, then dilute to 100 or 150 c.c.

Sulphuric Acid (dilute). — Twenty per cent strong H_2SO_4 in distilled water.

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INTERNATIONAL ATOMIC WEIGHTS, 1922

O = 16

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
Aluminium	Al	27.0	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.9	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Nitron	Nt	222.4
Bismuth	Bi	209.0	Nitrogen	N	14.008
Boron	B	10.9	Osmium	Os	190.9
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Calcium	Ca	40.07	Phosphorus	P	31.04
Carbon	C	12.005	Platinum	Pt	195.2
Cerium	Ce	140.25	Potassium	K	39.10
Cesium	Cs	132.81	Praseodymium	Pr	140.9
Chlorine	Cl	35.46	Radium	Ra	226.0
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.1	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.
Dysprosium	Dy	162.5	Scandium	Sc	45.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.1
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	70.1	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulphur	S	32.06
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.00	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.15
Indium	In	114.8	Thulium	Tm	169.9
Iodine	I	126.92	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.2
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium	Yb	173.5
Lutecium	Lu	175.0	(Neoytterbium)		
Magnesium	Mg	24.32	Yttrium	Yt	89.33
Manganese	Mn	54.93	Zinc	Zn	65.37
Mercury	Hg	200.6	Zirconium	Zr	90.6

Compiled by the International Committee on Atomic Weights consisting of F. W. Clarke, T. E. Thorpe, and G. Urbain. J. Am. Chem. Soc., **43**, 1751.

